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THE KINETICS OF THE THERMAL ISOMERIZATION OF THE PINENES

By

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PREFACE

The rates of the thermal isomerization of the pinenes, and nature of the products formed, allow the proposal of the simple mechanism developed in this paper. The mechanism merely involves the breaking of a strained structure in the form of a cyclobutane ring at a weak point where a carbon atom is linked to four other carbon atoms and in the beta position to an unsaturated carbon.

Mosher has shown that the reactions of alpha and beta pinene in the presence of acidic materials (proton donors) can be explained in terms of the Whitmore carbonium ion mechanism. They form the same ion intermediate and this accounts for the fact that they form the same products, though not necessarily in the same proportions. With each of these compounds the rate of reaction depends upon the concentration of both the protons and the terpene. Therefore, change in concentration of either should change the rate of the reaction.

The thermal isomerization products of alpha pinene and beta pinene are not identical although they are noticeably similar, and are not the ones obtained in the presence of proton donors. The study of the kinetics of the thermal isomerization of alpha pinene by Fuguitt and Hawkins (15) in this laboratory did not involve a change of the initial concentration of alpha pinene and did not provide for changes in possible sources of protons in the reaction mixture. The results showed that the reaction was a first order process. The mechanism developed herein is in conformity with this fact. [The present work includes a mechanism for the thermal isomerization of both alpha and beta pinene. To obtain information to establish the order of the reactions, changes were made in the concentration of the pinenes by dilution with dipentene. To determine whether or not the mechanism of the thermal reaction involved a proton, reactions were conducted in the presence of a weak acid and a weak base. Additions of an antioxidant and the diluent showed that chain reactions and peroxide mechanisms are not applicable. The evidence indicates that the reactions are probably unimolecular.]

The course of the reactions, as reported by Fuguitt and Hawkins, indicates that alloocimene is a primary product in the isomerization of alpha pinene. The mechanism postulated here requires ocimene to be a primary product which in turn isomerizes to alloocimene. This is in line with the work of Enklaar who showed that ocimene is quite readily converted to alloocimene upon heating. While ocimene was not found as a product when alpha pinene was heated for the stated lengths of time in the liquid phase, it was obtained when alpha pinene vapors were heated for very short periods.

The mechanism proposed herein accounts for the various products of isomerization of both alpha and beta pinene.

Additional study of the polymerization of allo-ocimene is included.

CHAPTER I

THE THERMAL ISOMERIZATION OF ALPHA PINENE

Review of Previous Work

The study of this reaction began with the work of Berthelot and his contemporaries about 1853 (1,2). They sealed French turpentine in glass ampoules and observed that at 250 to 300° it changed its density, optical rotation and boiling point, that no gas was given off, and that polymers were formed. In 1885 Wallach (3), showed that French turpentine produced dipentene at 250 to 270°. The tetrabromide was used as the identifying derivative. He also noted the fact that polymers were formed. Figure 1, page 5,shows the structures of the compounds involved in the reaction.

In searching for a first order gaseous racemization, D. F. Smith in 1927 (4) decided to study the thermal isomerization of alpha pinene. Apparently it was not suspected that alpha pinene was the major constituent in the turpentines used by Berthelot and Wallach, and the change in optical rotation of alpha pinene at elevated temperatures was attributed to racemization. The rate of change of optical rotation was measured and comparison made of the rates for the supposed racemization in the gas and liquid

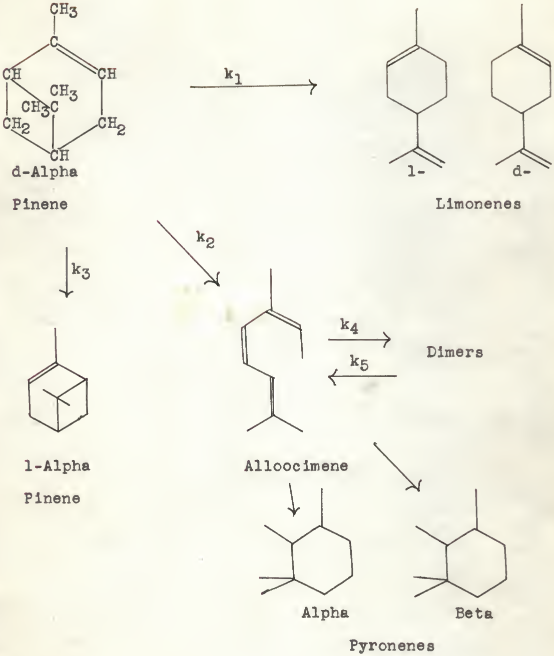


FIGURE 1. THERMAL ISOMERIZATION OF ALPHA PINENE AT 189.5 AND 204.5°

phases, for solutions of alpha pinene in petrolatum, acetophenone, and a-methyl naphthalene. Five fold changes of concentration in the gas phase had very little effect, and the gas phase rate constant was found to be about two thirds that of the liquid phase constant. The fact that the products of this reaction boiled about four degrees higher than the original pinene, and that the first and last fractions were found to have different rotations was attributed to a slow side reaction, perhaps forming limonene.

Smith was chiefly interested in the mathematical treatment, but the organic chemists Conant and Carlson were familiar with Wallach's work and doubted the simplicity of the reaction. They reported in 1929 (5) that efficient separation of alpha pinene and dipentene was difficult with the rectification apparatus at their disposal, but that a fairly accurate determination of the amount of each in a mixture of the two could be made by catalytic hydrogenation, because dipentene takes up two moles of hydrogen while alpha pinene takes up one. This method gave fair agreement with the change in optical rotation. When the optical activity was 95% destroyed in a sample of alpha pinene, and the polymers separated by distillation, it was found that the resulting mixture was nearly pure dipentene, if the hydrogenation method was reliable. Very good yields of dipentene tetrabromide could be obtained from it.

Conant and Carlson were interested in the products rather than the rate, but they obtained values of from 4 to 23 x 10^{-5} for a first order reaction constant at 200° or so. Smith's work indicated a gas phase rate constant for racemization of about 8.6 x 10^{-5}, with activation energy of about 43,700 calories per mole. In 1930 Kassel (6) called attention to the fact that, since it was an isomerization rather than a racemization, the value was double that given by Smith, or about 17 x 10^{-5}.

Thurber and Johnson (7), also called attention to this error in the calculation of the rate constant when they reported isomerization of pinene from two sources. They attempted to demonstrate a difference in isomeric form of the pinenes by comparison of activation energy required to bring about isomerization. They used a method of measuring rate constants very similar to that of Smith. Their results are not of great value because their original materials are not sufficiently described to make possible an estimate of their purity. Efficient distillation columns were not generally available at this time, although they became common in the next few years.

In 1933 and 1934 Arbusov (8,9) reported a new angle of attack. He passed alpha pinene through tubes maintained at 240-250° and found that considerable amounts of allo-ocimene were present in the isomerization product. Dupont and Dulou in 1935 (10) used a copper tube packed with copper gauze and obtained dipentene, alloocimene, and alpha and beta pyronenes. This was confirmed by Goldblatt and Palkin (11) using a glass tube maintained at 375°. The latter further demonstrated that the pyronenes were produced from alloocimene at 300° or above (12). The liquid phase isomerization of alpha pinene between 190° and 285° was reported by Fuguitt and Hawkins in 1945, using glass ampoules, and the reversible formation of dimers of allo-ocimene noted (13). The dimers explained the polymer obtained by previous workers. A continuous liquid phase isomerization process was described by Savich and Goldblatt in 1946 (14), in which short contact times and high temperatures were used. Alpha pinene was shown to produce the same products in about the same proportion as in the gas phase reaction.

A study of the rates of liquid phase isomerization of alpha pinene in glass ampoules at 189.5° and 204.5° by Fuguitt and Hawkins was published in 1947 (15). The rates of formation of dipentene and alloocimene and the activation energies were determined, and in addition the rate of racemization of alpha pinene was shown to be appreciable, though much smaller than either isomerization rate. Further, isomerization reactions and racemization were shown to follow the pattern for first order reactions, although the constants did not agree particularly well with the data of Smith, as they were somewhat higher.

The reaction rates for the dimerization of the alloocimene and the decomposition of the dimer, and the heats of activation were reported by Fuguitt in 1943 (16). Figure 1 shows the structure of the products of the thermal isomerization. The labelled constants are the specific reaction rates determined by Fuguitt and Hawkins.

Carbonium Ion Theory

Mosher, in 1947 (17), reviewed work involving the isomerization of the pinenes in the presence of some proton donors and applied the Whitmore carbonium ion mechanism to the Wagner-Meerwein rearrangements found under these conditions. He stated that this mechanism was not satisfactory to explain the products of the thermal isomerization of alpha and beta pinenes. The carbonium ion mechanism requires that both alpha and beta pinene have the same primary intermediate. Illustrations of this mechanism are shown in Figure 2, page 10. It is obvious that the products do not approximate those obtained from alpha pinene by thermal isomerization.

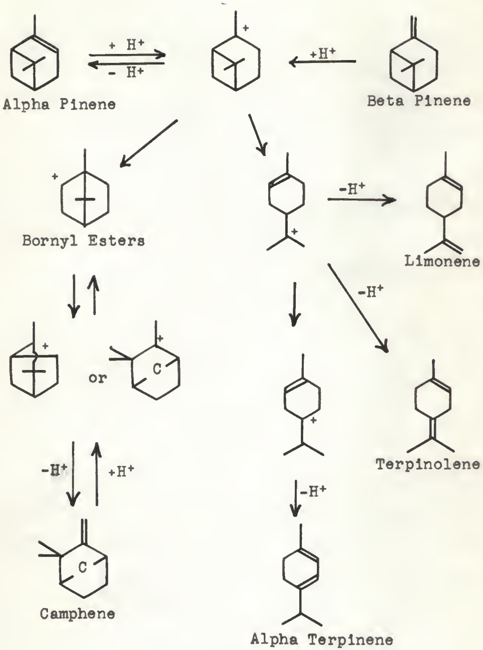


FIGURE 2

CARBONIUM ION MECHANISM FOR THE CATALYTIC ISOMERIZATION OF ALPHA PINENE

If the carbonium ion mechanism is involved in the thermal isomerization of alpha pinene, a change in either concentration of protons available or in the concentration of the pinene should show some effect on the rate of isomerization to the limonenes and alloocimene.

The work of Fuguitt and Hawkins (15) shows that the isomerization of alpha pinene follows the first order equation within the limits of experimental errors. However, change in initial concentration of alpha pinene, or of the nature of the solution to alter the concentration of protons available, was not made. Thus it was possible that the reaction was actually bimolecular, with the concentration of protons staying approximately constant, and thus appearing to be a first order reaction.

Effect of Dilution, Mild Acids and Base, and Antioxidant

In this study the concentration of alpha pinene and beta pinene was reduced to half its concentration in the pure state by dilution with dipentene, which is not isomerized by heating at the temperatures used (18). Table 1, page 12 shows that the reaction follows the first order course and gives approximately the same constant reported by Fuguitt and Hawkins (15). The same rate constant and the same first order course is shown by the isomerization in the presence of the proton acceptor (quinoline) in

TABLE 1

Alpha Pinene at 204.5° in Dipentine

k_1 for dl-Limonene and k_2 for Alloocimene in

First Order Equation

Expt. No.	% Pinene	t (min)	k_1	k_2	$k_1 + k_2$
H 112	48.5	817	2.0	1.3	3.3
H 113	48.5	817	2.2	1.5	3.7
H 116	48.5	2200	1.8	1.2	3.0
H 117	48.5	2200	2.0	1.2	3.2
H 114	48.5	3600	1.9	1.2	3.1
H 115	48.5	3600	2.1	1.2	3.3
H 52	49.0	5400	2.0	1.3	3.3
H 53	49.0	5400	2.3	1.7	4.0
Average			2.0	1.3	3.3
Average Deviation			5.6%	9.6%	6.3%
Fuguitt and Hawkins			2.4	1.2	3.6

Table 2, page 14,and in the presence of proton donors (benzoic acid and hydroquinone) in Table 3, page 14 and Table 4, page 15. Details of experimental methods are given in Appendix I, page 87, and calculations are shown in Appendix II, page 104.

The hydroquinone would also have had an effect if the reaction were pseudo unimolecular in the observed ranges of concentration where actually a chain reaction involving oxygen absorbed from the air was present.

The rate constant for the disappearance of alpha pinene will be observed to agree fairly well with the value reported by Fuguitt and Hawkins, which is 3.6×10^{-4}. However it will be noted that the values for k_1 and k_2 depart somewhat from the values previously reported.

In contrast to the method of Fuguitt and Hawkins, who sealed alpha pinene into evacuated ampoules as it was taken from the distilling column, a large sample was collected over a period of months and was stored under nitrogen. This uniform specimen was then used to fill ampoules, with considerable care being taken to exclude air. That the precautions were not completely adequate is demonstrated by the results shown in Table 5, page 16.

The first two results shown are from samples of freshly distilled alpha pinene. The next pair are from the same specimen as the proceeding pair sealed in an

TABLE 2

Alpha Pinene at 204.5° with 1% Quinoline Added

k_1 for dl-Limonene and k_2 for Alloocimene in First Order Equation

Expt. No.	t (min)	$k_1 \times 10^4$	$k_2 \times 10^4$	$k_1 + k_2 \times 10^4$
H 152	3010	2.4	1.1	3.5
H 153	3010	2.3	1.1	3.4
H 58	6800	2.0	1.4	3.4
H 59	6800	2.0	1.3	3.3
Average		2.2	1.2	3.4
Average Deviation		8.0%	10.4%	1.5%
Fuguitt and Hawkins		2.4	1.2	3.6

TABLE 3

Alpha Pinene at 204.5° with 1% Benzoic Acid Added

k_1 for dl-Limonene and k_2 for Alloocimene in First Order Equation

H 64	1400	2.1	1.9	4.0
H 154	3010	2.5	1.1	3.6
H 65	4970	2.2	1.5	3.7
H 155	6700	2.4	.9	3.0
Average		2.3	1.3	3.6
Average Deviation		6.5%	27%	7.6%
Fuguitt and Hawkins		2.4	1.2	3.6

TABLE 4

Alpha Pinene at 204.5° with Hydroquinone Added

k_1 for dl-Limonene and k_2 for Alloocimene in

First Order Equation

Expt. No.	% Hydro-quinone	t (min)	$k_1 \times 10^4$	$k_2 \times 10^4$	$k_1 + k_2 \times 10^4$
H 56	1.0	1500	2.1	1.9	4.0
H 57	1.0	1500	1.9	1.7	3.6
H 36	1.0	6600	2.1	1.2	3.3
H 39	1.0	13750	2.0	1.4	3.4
H 40	1.0	13750	1.8	1.2	3.0
H 60	0.1	6800	1.8	1.4	3.2
H 61	0.1	6420	2.1	1.3	3.4
Average			2.0	1.4	3.4
Average Deviation			5.7%	14%	6.2%
Fuguitt and Hawkins			2.4	1.2	3.6

TABLE 5

Alpha Pinene at 204.5°

k_1 for dl-Limonene and k_2 for Alloocimene in

First Order Equation

Expt. No.	Age of Sample	t (min)	$k_1 \times 10^4$	$k_2 \times 10^4$	$k_1 + k_2 \times 10^4$
Fuguitt and Hawkins Average			2.4	1.2	3.6
H 24	1 month	5090	2.2	1.0	3.2
H 25	1 month	5090	2.3	.9	3.2
H 54	12 months	7875	2.1	1.2	3.3
H 55	12 months	7866	2.1	1.3	3.4
H 62	13 months	5060	2.2	1.3	3.5
H 63	13 months	5060	2.1	1.4	3.5
H 66	2 days	5030	2.0	1.0	3.0
H 67	2 days*	4920	2.0	1.4	3.5

* Wet air was bubbled through sample for 1 hour, it stood five hours before evacuation and sealing in ampoule.

ampoule after storage under nitrogen for a year, and the third pair are from the same sample after thirteen months.

The last pair of experiments were made with a sample of freshly distilled alpha pinene that was divided into two parts. One part was sealed in an evacuated ampoule immediately, the other had air saturated with water vapor blown through it for an hour. It was allowed to stand, open to the air, for five hours before it was evacuated and sealed. Both were heated immediately after sealing.

A patent by Martin (19) reported water as a catalyst for the isomerization of alpha pinene, where an equal volume of water and terpene were stirred together in a steel autoclave. An experiment was tried using an Aminco high pressure rocking bomb. Equal quantities of alpha pinene and water were heated, with constant rocking, to 225° in 75 minutes, held at that temperature for 135 minutes, and cooled to 40° in 90 minutes. This would indicate that the actual reaction time was equivalent to about 140 minutes at 225°. The terpenes were dried and carefully fractionated. The recovery of 76% of the weight of the dried terpenes as alpha pinene with $n_D^{23} = 1.4638$ shows

$$k_1 + k_2 = \frac{2.3}{140} \log \frac{100}{76} = .002$$

From Fuguitts work at 189.5° and 204.5°, $k_1 + k_2$ at 225° should be about .003. Apparently the presence of water alone does not greatly change the rate at which alpha pinene disappears.

Conclusions

From the results with pure alpha pinene stored under nitrogen it does not appear particularly important that freshly distilled material be used. Blanks of the material should be used during the progress of the work when various additions to the reaction mixture were being tried.

The conclusion from Tables 1 to 5 is that the rate of disappearance of alpha pinene in thermal isomerization is such as to indicate that the reaction is unimolecular. Details of experimental techniques are discussed in the Appendix I, page 87, and calculations are shown in Appendix II, page 104.

CHAPTER II

THE THERMAL ISOMERIZATION OF BETA PINENE

Review of Previous Work

Thermal isomerization of 1-beta pinene (1-nopinene) by passage of the vapor through a Pyrex glass tube at 400° was reported by Goldblatt and Palkin in 1941 (11). They found 1-limonene and myrcene to be the main products, with some of the myrcene polymer, alpha camphorene, also being formed. These products are shown in Figure 3 on page 20. This work corrected an earlier report by Arbuzov (9) that alloocimene was formed in the reaction.

The products here formed are somewhat similar to those from alpha pinene in Figure 1, but unlike those predicted from the carbonium ion mechanism proposed by Mosher for catalysed reactions of beta pinene in Figure 2, page 10.

Rates of Isomerization

As in the case of alpha pinene, it was desired to determine the order of reaction best fitting the thermal isomerization of beta pinene under various conditions. Samples of 1-beta pinene were sealed in evacuated ampoules and kept for various lengths of time at constant temperatures at which the reaction proceeds at a convenient rate.

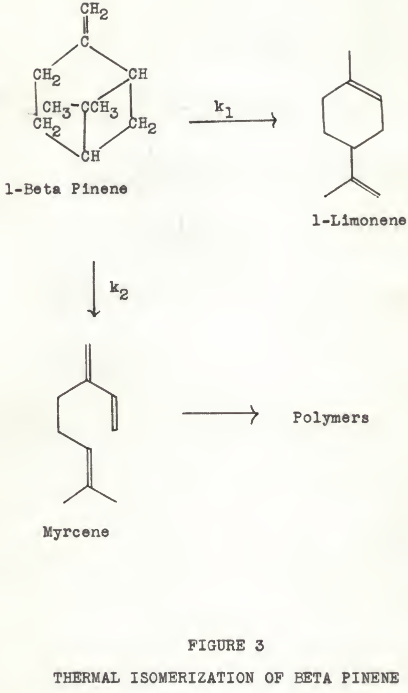


FIGURE 3

THERMAL ISOMERIZATION OF BETA PINENE

at 400°

The proportion of unreacted beta pinene in each sample was determined by distillation. Experimental details are given in Appendix I. Tables 6 and 7, page 22, show the results of two series of determinations at different temperatures, together with the specific reaction rate constants calculated for a first order reaction. It appears that the reaction is first order under these conditions, and that the reaction is slower than the isomerization of alpha pinene under comparable conditions.

It must be noted that the reaction rates are given in terms of time in minutes to conform with the results of the study of alpha pinene and with the work of Fuguitt and Hawkins.

The average values of k_1 and k_2 from Tables 6 and 7 were used in the Arrhenius equation, integrated between the limits of the temperatures of isomerization, to obtain the activation energies for the two isomerization reactions. The integrated form of the same equation was used to solve for the logarithm of the integration constant s, the collision frequency per second. The value of the activation energy E for the formation of limonene is 50,000 calories per mole, and the logarithm of the collision frequency s is 16.2. The energy of activation for the formation of myrcene from beta

TABLE 6

Beta Pinene at 219.5°

k_1 for Formation of Limonene, k_2 for Myrcene-Polymers in First Order Equation

Expt. No.	Time (min.)	$k_1 + k_2 \times 10^4$	k_1/k_2
H 161	760	1.9	
H 162	760	2.3	
H 163	1500	2.2	
H 164	1500	2.2	
H 165	2900	2.1	.45
H 166	2900	2.1	.44
H 167	5230	2.1	.46
H 168	5230	1.9	.39
Average		2.1	.435
Average Deviation		3.6%	5.0%

$k_1 = .64 \times 10^{-4}$ $k_2 = 1.46 \times 10^{-4}$

TABLE 7

Beta Pinene at 234.5°

H 214	170	9.6	
H 215	170	9.5	
H 216	360	8.7	
H 217	360	9.3	
H 209	770	8.4	.42
H 210	770	9.2	.49
H 211	1313	8.8	.48
H 212	1313	8.6	.49
Average		9.0	.47
Average Deviation		4.3%	5.3%

$k_1 = 2.9 \times 10^{-4}$ $k_2 = 6.1 \times 10^{-4}$

pinene is 47,000 calories per mole, and log *s* is 15.4.

Details of the calculations are given in Appendix II, Table 24, page 124.

Effect of Dilution, Acid, Base and Antioxidant

The results of heating a mixture of beta pinene diluted with an equal weight of limonene are shown in Table 8, page 24, where the temperature is the same as that used for the series of reactions shown in Table 6, page 22. Again the first order treatment is adequate, and although the difficulty of separating the beta pinene from the limonene is greater than in the preceeding determinations, the constant agrees fairly well with that obtained for pure beta pinene.

Two series of beta pinene samples, one containing one percent quinoline and the other one percent hydroquinone, were maintained at the same temperature as the series shown in Table 6, page 22, and Table 8, page 24. The results are shown in Table 9, page 24, and Table 10, page 25. With these two series were heated a pair of samples of pure beta pinene. The two series show that mild acidic or basic conditions in the reaction mixture do not affect the rate of the reaction, and that the reaction is still first order.

Preliminary tests of the effect of small concen-

TABLE 8

Beta Pinene at 219.5°

Diluted With an Equal Weight of Dipentene

k_1 for Reaction Producing Limonene, k_2 for

Myrcene-Polymer in First Order Equation

Expt. No.	Time (min.)	$k_1 + k_2 \times 10^4$
H 169	760	2.4
H 170	1500	2.5
H 171	2900	2.3
H 172	5230	2.0
Average		2.3
Average Deviation		6.5%

TABLE 9

Beta Pinene With 1% Quinoline Added at 219.5°

H 192	750	3.1
H 193	1460	2.6
H 194	2900	2.4
H 195	4340	2.5
H 196	5780	2.5
H 197 (Blank)	2900	--- (2.4)
Average		2.6
Average Deviation		6.9%

TABLE 10

Beta Pinene With 1% Hydroquinene Added at 219.5°
k_1 for Reaction Producing Limonene, k_2 for
Myrcene-Polymer in First Order Equation

Expt. No.	Time (min.)	$k_1 + k_2$ x 10^4
H 198 (Blank)	2870	--- (2.6)
H 199	715	2.4
H 200	1430	2.6
H 201	2870	2.6
H 202	4310	2.3
H 203	5760	2.4
Average		2.5
Average Deviation		4.8%

trations of benzoic acid on beta pinene showed that some alpha pinene was formed. This indicates that benzoic acid will provide protons to react with beta pinene to form the carbonium ion common to both alpha and beta pinene, and that the carbonium ion loses a proton to yield alpha pinene. This mechanism is shown in Figure 2, page 10. Since this study is concerned with thermal isomerization only, further study of the effect of benzoic acid was not undertaken.

Myrcene and Polymers

The work of Goldblatt and Palkin (11) in the gas phase and at higher temperatures showed that, in addition to limonene, myrcene and its polymer, alpha camphorene, were formed in the isomerization of beta pinene. In this study in the liquid phase, the reaction produces a characteristic gummy solid that separates out of the reaction mixture on cooling to room temperature, and considerable amounts of compounds boiling at about 200° at 20 mm, which are liquid at room temperatures. This boiling point is approximately that of alpha camphorene, 179-180° at 8.5 mm (21). Myrcene is present only in extremely small amounts, if at all, in this reaction mixture. This set of circumstances suggests that the myrcene has reacted to form polymers.

Myrcene has been found to form polymers at elevated temperatures (20,21). They consist of alpha camphorene and other dimers and a material which is a "viscid gum" at room temperature, corresponding to the polymeric material obtained in the isomerization of beta pinene. Myrcene polymerization rates have been studied by Lebedev (22) and by Gapon (23) at 150°. The data of Lebedev was used in the calculations in Table 11, page 28, to determine a rate constant for the polymerization. Making the assumption that in 1913 Lebedev did not have efficient distilling columns at his disposal and that his myrcene was only about 80% pure, the constant for the reaction at 150° was approximately .0014. In the case of polymerization of alloocimene at 189.5° the constant was about .0008. Thus it is clear that myrcene polymerizes much more readily than alloocimene.

Myrcene is so much more reactive than either beta pinene or limonene, that the polymers formed were considered to not contain any of these compounds. In the absence of a better method of determination, the weight of polymers has been taken as the weight of myrcene formed from beta pinene. The only products in the reaction mixtures, in addition to the polymers, were l-beta pinene and l-limonene. Calculations of the rate constants for production of limonene and myrcene are based on the ratio

TABLE 11

Rate of Polymerization of Myrcene

Data from Lebedev as Quoted by Egloff (24)

Temperature at 150°

Data		Calculations		
Time (hours)	% Polymer	Time Min.	k Assuming 100% Purity	k Assuming 80% Purity
4.5	53	270	.0008	.0014
13.5	68	810	.0005	.0013
115	78	6900	.0001	.0011
288	82.5	17280	.00004	---

$$k = \frac{1}{at} \frac{x}{a-x}$$

From Similar Densities for Alloocimene and Myrcene

$$d_{20^\circ} = .806, \; d_{204.5^\circ} = .66$$

$$d_{150^\circ} = .71$$

$$a = 5.2$$

of limonene and polymer found, and the rate constant of the disappearance of beta pinene.

Summary

The isomerizations of beta pinene to limonene and myrcene are first order reactions, the constants of which are listed below

	k_1 Beta Pinene $\longrightarrow$ Limonene	k_2 Beta Pinene $\longrightarrow$ Myrcene
k's at 219.5° (in minutes -1)	0.64×10^{-4}	1.46×10^{-4}
k's at 234.5° (in minutes -1)	2.9×10^{-4}	6.1×10^{-4}
Activation Energy Calories/Mole	50,000	47,000
Log s (in seconds $^{-1}$)	16.2	15.4

CHAPTER III

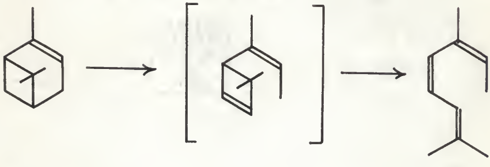
A MECHANISM FOR THE ISOMERIZATION OF THE PINENES

The rates of disappearance of alpha and beta pinenes under various conditions indicate that the isomerizations are first order reactions. The structures of, and products from, the two pinenes are somewhat similar. It may be that the courses of the reactions are different only as is required by the different position of the double bond in the two molecules.

Arbuzov Mechanism for Allocimene

A mechanism, suggested by Arbuzov in 1934 (25), for the formation of allocimene for alpha pinene is shown in Figure 4. However this does not account for dipentene and for racemization of alpha pinene.

FIGURE 4



Beta Pinene

In thermal isomerization the increase in thermal energy in a molecule causes increased vibration of the electrons and atoms. Because electron motion requires less energy than extensive motion of atoms it must be considered first. If the electron motion in the double bond in beta pinene causes an increase in electron density around carbon 7 in II of Figure 5, page 32, there is a corresponding positive charge on carbon 1. This tends to draw toward carbon 1 a pair of electrons from neighboring carbon atoms. The most susceptible pair is the one which lies between carbon 6 and the quaternary carbon 8. This is so because a carbon to which is attached four alkyl groups repels electrons to a greater extent than a carbon attached to three or less alkyl groups, the other bonds being to hydrogen atoms. When the two electrons forming the bond to the quaternary carbon move toward carbon 6, the strained cyclobutone ring tends to open, separating carbon 6 and carbon 8. As a result of the positive charge on carbon 1 a double bond may form between carbons 6 and 1 as shown in III. Resonance produces the form IV with a negative charge in the ring. The positive and negative charges are then adjacent and recombination to form beta pinene can take place.

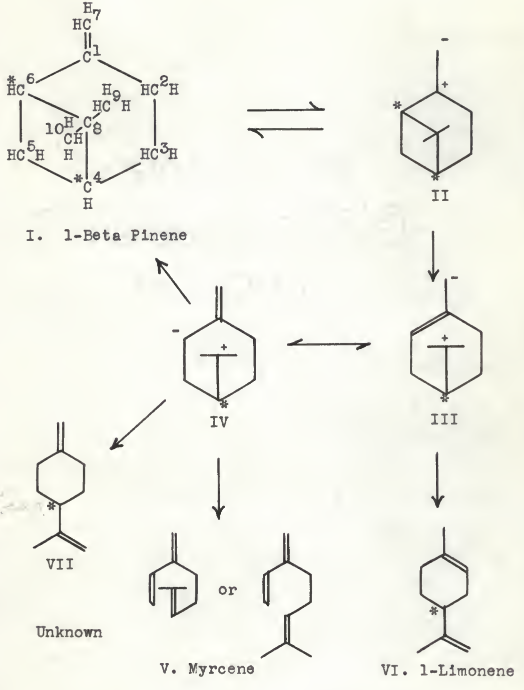


FIGURE 5. MECHANISM FOR THE THERMAL ISOMERIZATION OF BETA PINENE

It is also possible for the positive charge on carbon 8 to attract an electron pair from the adjacent carbon 4 in the chain. At the same time the negative charge on carbon 6 repels the electrons on carbon 5. The electron pair between carbons 4 and 5 is subjected to both effects. The result is that this pair may move to the position between carbons 4 and 8. The electron pair forming the negative charge on carbon 6 moves into position between carbons 5 and 6 to form another double bond. This produces myrcene, V.

The formation of l-limonene, VI, from l-beta pinene results when the resonance form III shifts a proton from carbon 9 or 10 to carbon 7. The planar representation given in the figure does not indicate that this is readily possible. However, by use of a three dimentional configuration, such as a slightly altered Fisher-Hirshfelder model, it is demonstrated that the distance between the hydrogen atoms on carbon 9 or 10 and carbon 7 is considerably less than indicated by the planar figure.

The beta pinene used was optically active. The active carbon atoms are marked in the figure. In the formation of limonene the configuration about carbon 6 was changed in such a way that its activity was destroyed. The configuration of the optically active carbon 4 did not change, and this accounts for the formation of an optically active limonene as expected. The l-beta pinene produced l-limonene in this work, which is in agreement with the findings of Goldblatt and Palkin (11).

There is a possible new terpene hydrocarbon, VII, that may form from IV by transfer of a proton from carbon 10 to carbon 6. This seems rather unlikely and no such hydrocarbon has been reported from this reaction. No search for it was made in this work. As the known products amount to 98% of the original beta pinene, it was not felt that further search was justified.

Alpha Pinene

The thermal isomerization of d-alpha pinene appears to be more complicated. It has been shown (15) that the process includes racemization of the alpha pinene as well as the formation of dl-limonene and alloocimene. Thus a more extensive explanation is required than that necessary to account for the products obtained from beta pinene.

The recemization may be pictured, in Figure 6, page 35, as quite similar to the type of mechanism used in the case of beta pinene. The thermal movement of the electron pairs in the double bond of alpha pinene, VIII, alternately puts a positive charge on the adjacent carbons

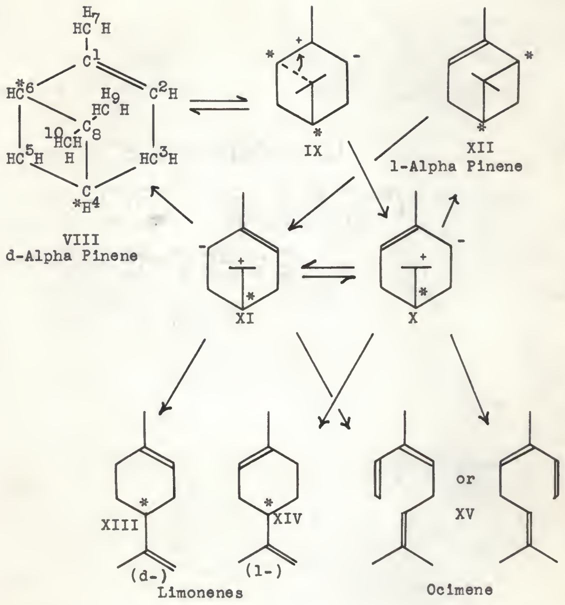


FIGURE 6

MECHANISM FOR THE THERMAL ISOMERIZATION OF ALPHA PINENE

3 and 6. The pair of electrons connecting carbon 6 to the quaternary carbon 8 is repelled by the other three alkyl groups on the quaternary carbon 6, so when the pairs of electrons in the double bond between carbons 1 and 2 approach 1 there is only an increase of the electron density around carbon 6, with no significant changes in bonds. However, when the electron density around carbon 2 increases, carbon 1 becomes positively charged, IX, and this then permits the pair of electrons which are repelled by carbon 8 to form a double bond between carbons 1 and 6. Simultaneously the bond between carbons 6 and 8 is broken, X, and the cyclobutane ring tends to open. The resonance forms X and XI, involving an allylic shift, makes possible the recombination of carbon 8 with either carbon 2 or 6 to form d- or l-alpha pinene. The forms X and XI, and also VIII and XII, are mirror images, and hence represent optical isomers. This accounts for the decrease in optical activity noted by Fuguitt and Hawkins (15).

The formation of the limonenes, XIII and XIV, in equal amounts (dipentene) is accounted for by an equally probable proton shift from carbon 9 to carbon 2 or from carbon 10 to carbon 6, due to the allylic shift in the ring. In this case the distance between the hydrogen atoms on carbons 9 and 10 and the negatively charged carbons 2 and 6 is shorter than the distance involved in the case of the beta pinene isomerization where a proton moves from carbon 9 or 10 to carbon 7. This accounts for the fact that the fraction of alpha pinene converted to dipentene is greater than the fraction of 1-beta pinene converted to 1-limonene.

The allylic shift in beta pinene isomerization involves the exocyclic carbon 7 and hence no dipentene can form and the optical activity of the limonene is of the same sign as that of the original beta pinene.

Ocimene-Alloocimene

The resonance forms X and XI have a negative charge in the ring and a positive charge on carbon 8. By the mechanism applied in the case of the formation of myrcene from beta pinene, a pair of electrons between carbon 4 and carbon 3 of X, or carbon 4 and carbon 5 of XI, shifts into the position between carbons 4 and 8 to form a double bond. In both cases ocimene, XV, results.

Previous workers have found no trace of ocimene, but have found large amounts of alloocimene. This mechanism predicts that the primary product is ocimene. Enklaar (26) has stated that ocimene is readily converted to alloocimene at its boiling point of about 170°. If this is true, the higher temperatures necessary to isomerize alpha pinene should cause the immediate isomerization of the ocimene to alloocimene and thus account for the presence of the latter. To clarify this point the work in the next chapter was undertaken.

Rice Free Radical Mechanism

Rice wrote in 1935 (27) that the product of thermal isomerization of alpha pinene should be ocimene. His mechanism, based on the free radical theory and the concepts of that time as to bond strengths, is shown in Figure 7, page 39.

The free radical mechanism requires the separation of pairs of bonding electrons. The formation of both optical isomers of limonene and the racemization of alpha pinene involve the free radical version of the allylic shift. In this shift the free radical II has a double bond between the carbons which are in the alpha and beta positions with reference to the carbon holding the lone electron. This double bond is assumed to have the ability to separate one of its bonding pairs of electrons to give the structure shown in IV, a four fold free radical. Reformation of bonds will thus give a racemic mixture.

It must be noted that the formation of limonene involves the shift of atomic hydrogen, and that the type of free radical shown here should produce linear polymers of a molecular weight greater than double that of alloocimene.

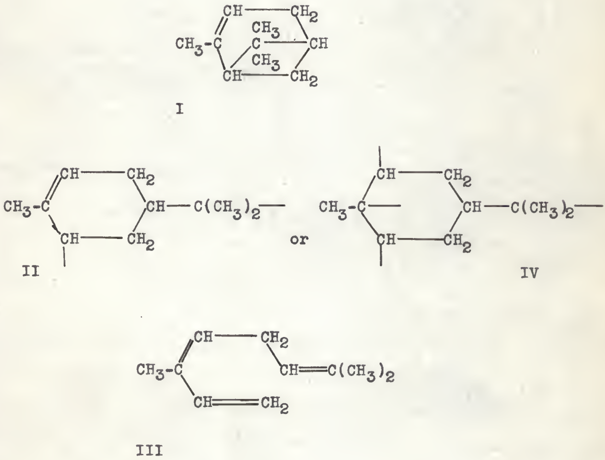


FIGURE 7

THE DECOMPOSITION OF ALPHA PINENE TO FORM OCIMENE

CHAPTER IV

OCIMENE

To conform to the mechanism for the isomerization of alpha pinene as reported in Chapter III, ocimene rather than the previously reported alloocimene must be the primary product.

The formation of ocimene is difficult to prove because it has not been, and probably cannot be, isolated from the products of isomerization at the temperatures and reaction times used in this study. This is due to the fact that it is very readily isomerized to alloocimene (26) by heating, even at temperatures as low as 150°, which is well below the temperatures at which alpha pinene isomerizes at a reasonable rate. Since no significant amount of unaccounted for material has been reported by Fuguitt and Hawkins (15) or by Fuguitt (16) there was no need to rework the products of liquid phase isomerization at 200°. Goldblatt and Palkin reported small amounts of unidentified terpenes in the gas phase isomerization of alpha pinene when it was passed through a hot tube for short contact periods. This material may or may not have contained ocimene. There appears to be no literature reference covering the production of ocimene, except from natural sources. With these facts in mind, an apparatus was made in which alpha pinene vapor was passed over a hot wire and promptly chilled to prevent the further change of the ocimene formed.

Apparatus. The apparatus consisted of a wire grid made of several inches of 24 B. & S. guage nichrone wire bent back and forth in one plane to fill a square inch of area with parallel lengths about 5 mm. apart. This grid was suspended parallel to and about 7 mm. from a vertical, water-cooled, finger-type glass condenser. A 7 mm. id. glass tube ending an inch away from the grid served as a jet to direct the alpha pinene vapor through the grid to the condenser. The pressure in the apparatus was maintained at 20 mm. of mercury. Current in the grid was varied between 2.5 and 3.5 amperes in various experiments. It was found that a satisfactory and convenient adjustment of the wire temperature could be made by using just sufficient current to make the grid barely visible in a darkened room when no alpha pinene vapors were passing through it.

Because only a small part of the alpha pinene was converted at each pass over the grid, a recycling system was used. The condensate was led back to the bottom of the boiler, which was a 200 ml flask. Since ocimene is quite readily isomerized by heat, it must be kept from passing again over the grid. It boils about twenty degrees above the boiling point of alpha pinene, so a two foot length of 38 mm. id. Lecky-Ewell type (28) rectifying column was placed between the boiler and the grid. Adjustment of the amount of insulation at the top of the distilling column provided for the return of as much alpha pinene as reflux, at the start of an experiment, as was passed over the grid. As the isomerization proceeded the pot tepera-ture rose steadily from 55° to about 80°. Simultaneously the reflux ratio increased somewhat, which aided in preventing the ocimene from passing over the hot grid a second time. The temperature at the top of the rectifying column was allowed to rise only about one degree above that of alpha pinene, i. e. from 52.2 to 53.2°, at which time the charge was removed and fractionated. The lower the pressure in the system the lower the pot temperatures and the less would be the conversion of ocimene to alloocimene during the twenty four hour recycling process. The apparatus is sketched in Figure 8, page 43.

Several preparations were made. Each contained a substantial amount of alpha pinene, unchanged except in rotation. This racemization has been reported by Fuguitt and Hawkins (15). It was expected that the fraction boiling between 70 and 74° at 20 mm. would contain limonene

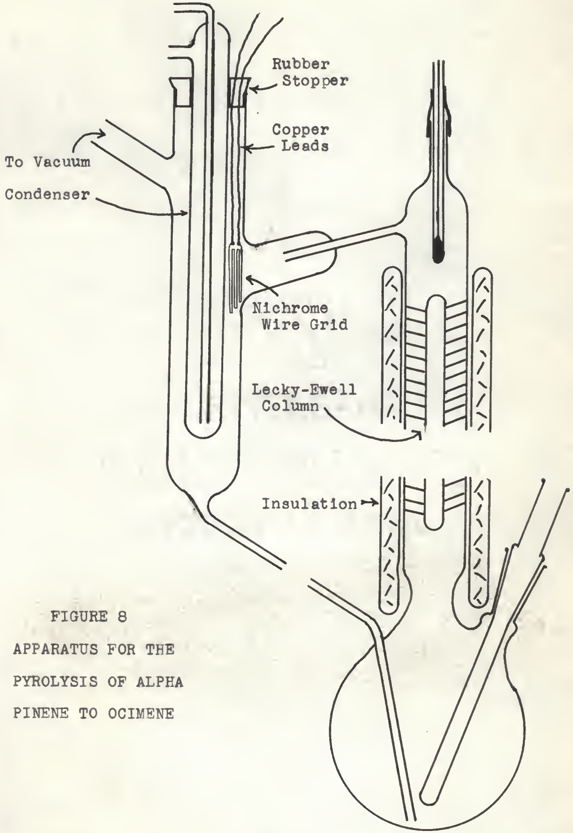


FIGURE 8

APPARATUS FOR THE PYROLYSIS OF ALPHA PINENE TO OCIMENE and ocimene, since limonene boils at about 71° and the boiling point of ocimene falls within this range at 20mm. Some alloocimene and polymers were also present.

Detection and Estimation. The detection, and estimation, of the ocimene was carried out by holding a few drops of the mixture at 204.5° for an hour in a small sealed ampoule and observing the change in refractive index.

Alloocimene showed a decrease in index of refraction when heated, due to polymerization. After an hour at 204.5° the index at 25° of one sample decreased from 1.5425 to 1.5380. Fuguitt showed that the refractive index of limonene-alloocimene mixtures varies almost linearly with composition, and that limonene is unchanged at these temperatures in the presence of alloocimene (13). On this basis the refractive index of the heated samples of ocimene-limonene can be used for measurement of the amount of ocimene present before heating. For the purpose of using these data to calculate the amount of ocimene obtained, it is assumed that the conversion of ocimene to alloocimene is practically instantaneous. This assumption is justified in view of the fact that the half life of ocimene at 204.5° is about 3 minutes.

To test this, a sample of ocimene-limonene mixture was carefully redistilled, and the fraction boiling between 70 and 73° at 20 mm. of mercury was taken. A fifty gram sample of this was held at 204.5° for an hour. Its refractive index after heating was 1.5020 at 25°. Assuming a linear relation between limonene (n_D^{25} = 1.4701) and the alloocimene products formed by an hour at 204.5° (n_D^{25} = 1.5380), there was 47% ocimene in the original sample. This calculation was verified by fractionation of this heated sample which produced 53% limonene and 47% alloocimene or its polymers.

A slightly more convenient method of approximating the amount of ocimene in mixtures that may also contain alloocimene is to observe the refractive index before and after heating. This involves the assumption of ideal behavior in the refractive index of solutions of limonene, ocimene, and alloocimene. The refractive index of ocimene may be obtained by extrapolation from the refractive index of limonene (1.4701) and the refractive index of the 47% ocimene and 53% limonene mixture (determined by analytical distillation after isomerization), which was found to be 1.4790. Assuming a linear relationship, the refractive index of pure ocimene is about 1.4890 at 25°. The refractive index of a mixture is the sum of the weight (or mole) fractions of the components multiplied by their respective refractive indices. If a is the weight fraction of ocimene, b of alloocimene, and c of limonene, then

$$1.4890a + 1.5420b + 1.4701c = n_D^{25} \text{ of mixture}$$

After an hour at 204.5°, this changes to

$$1.5380a + 1.5380b + 1.4701c = n_D^{25} \text{ after heating.}$$

Subtracting,

$$(1.5380-1.4890)a - (1.5420-1.5380)b =$$

$$0.0490a - 0.0040b = \text{Change in refractive index.}$$

In samples such as were produced in this work, the amount of alloocimene was small enough to make the term 0.0040b negligible. Hence the increase in refractive index of a sample held at 204.5° for an hour, divided by 0.0490, gives the mole fraction of ocimene originally present. The ocimene containing fraction of H 118 in Table 12, page 48, had a refractive index change of from 1.4773 to 1.4969 when held at 204.5°, for an hour, so (1.4969 - 1.4773)/0.0490 = 0.40. The various relationships of refractive index are shown in Figure 9, page 47.

Yields

Table 12, page 48, summarizes the important points of the preparations of ocimene. Yields up to 35%, on the basis of the amount of alpha pinene converted, were realized. Further work may raise that figure.

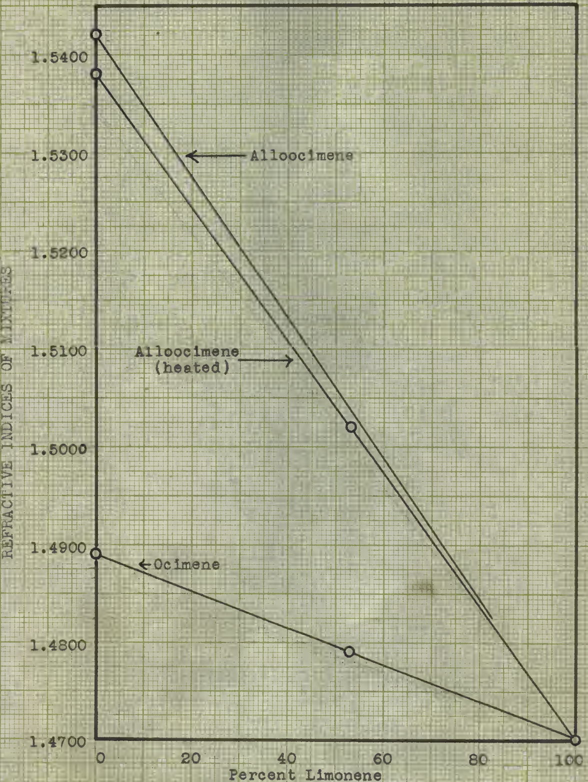


FIGURE 9. REFRACTIVE INDICES FOR ESTIMATION OF OCIMENE

TABLE 12

Ocimene Preparations

Expt. No.	Amps.	Drop/min. at Condenser	Residue (Allo + Polymer)	Alpha Pinene Isomerized
			g.	g.
H 118	2.2	10*	9.4	23.5
H 120	3.5	65	20.6	57.9
H 121	3.5	65	30.4	63.5
H 125	3.2	110	16.8	39.5
H 127	3.2	110	11.7	39.7
H 128	3.2	110	30.9	85.7

* 14 mm. id. Lecky-Ewell Column

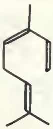
No.	Fraction boiling at 70-74° at 20 mm.						Yield **
	g	n_1	n_2	n_2-n_1	Ocimene		%
					%	g	
H 118	14.1	1.4773	1.4969	0.0196	40	5.6	24
H 120	37.3	1.4867	1.5006	0.0139	28	10.4	18
H 121	33.1	1.4791	1.4891	0.0100	20	6.6	10
H 125	22.7	1.4781	1.4988	0.0207	42	9.5	24
H 127	28.0	1.4790	1.5050	0.0260	53	14.8	37
H 128	54.8	1.4818	1.5062	0.0244	50	27.4	32

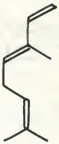
** On basis of alpha pinene isomerized

Boiling Points of Limonene-Ocimene Mixtures. During the careful fractionation at 20 mm. of the above sample for refractive index study, the temperature rose steadily from 71 to 74°. The column used was capable of exerting at least fifteen theoretical plates on the mixture. However, no good plateaus in the temperature vs. volume distilled plot were noted. The boiling point must be between 71 and 74° at 20 mm. because nothing distills below 71° and nothing is left at 74°. In an attempt to get a better separation the pressure was lowered to 5 mm. It was found that the mixture boiled over the range 51 to 54°. This did not improve the separation and hence the only advantage is a lower pot temperature and less isomerization of the ocimene to alloocimene.

There are two possible forms of ocimene, a cis and a trans at the central double bond, it is probable that, like alloocimene isomers, they boil at slightly different temperatures. Considering the source, there should be little of form II below.

I





II

Rate of Isomerization of Ocimene

Using an available mixture of ocimene with limonene, estimates were made of the rates of isomerization of ocimene at 159.5° and 189.5°. The index of refraction of the mixtures heated for various times were observed. The initial amount of ocimene was determined by observing the refractive index before and after heating this mixture for an hour at 204.5° and calculating as previously described on page 46. Samples consisting of a few drops of the mixture were placed in inch long ampoules of 6 mm. o. d. Pyrex tubing. Each tube was evacuated and sealed off. The ampoules were immersed in the oil bath for various times, cooled, opened, and the index of refraction of the contents observed. The data are shown in Table 13, page 51. The reaction fits the first order equation very well since the refractive index after complete conversion of ocimene to alloocimene is 1.5213. This corresponds to 71% alloocimene in the linear relationship between alloocimene and limonene, where pure alloocimene has a refractive index of 1.5420 at 25° (11). The change of refractive index method indicates 69% ocimene present originally, so about 2% alloocimene appears to have been present originally.

The rate constants are approximately 0.014 at

TABLE 13

The Isomerization of Ocimene to Alloocimene; Limonene-Ocimene Mixture, $n_D^{25} = 1.4832$ Before Heating

$n_D^{25} = 1.5163$ After 1 Hour at 204.5°

so 69% ocimene.

$$k = \frac{2.3}{t} \log \frac{C_o}{C_t} = \frac{2.3}{t} \log \frac{1.5213-1.4832}{1.5213-n} = \frac{2.3}{t} \log \frac{0.0381}{1.5213-n}$$

	Time min.	n_D^{25}	1.5213 - n	k
at 159.5°	9	1.4882	0.0331	0.016
	20	1.4925	0.0288	0.014
	41	1.4992	0.0221	0.013
	75	1.5083	0.0130	0.014
	160	1.5171	0.0042	0.014

$t_{\frac{1}{2}} = 49$ minutes

at 189.5°C	2	1.4900	0.0313	0.10
	4	1.4958	0.0255	0.11
	8	1.5042	0.0171	0.10
	16	1.5141	0.0072	0.10

$t_{\frac{1}{2}} = 0.69/0.10 = 6.9$ min.

$$E = \frac{2.3\ R\ T_2\ T_1}{T_2 - T_1} \log \frac{k_2}{k_1} = 25{,}950 \text{ cal/mole}$$

at 204.5°

$$\log \frac{k_3}{0.10} = 0.387 \qquad 2.4 = \frac{k_3}{0.10} \qquad k_3 = 0.24$$

$t_{\frac{1}{2}} = 0.69/0.24 = 2.9$ min.

159.5° and 0.10 at 189.5°. Extrapolating from these values, the half life at 204.5° is about 3 minutes. This explains why previous workers reported alloocimene and failed to find ocimene.

Ultraviolet Absorption Curves. A portion of the mixture of 53% limonene and 47% ocimene, as determined by analytical distillation after isomerization, was kept at 220° for 20 minutes. The absorption spectrum was taken, using a Beckmann DU Spectrophotometer, between 220 and 350 mu. The optical density curve is compared with that of an unheated portion of the mixture in Figure 10, page 53. The peak at 235 mu. is in the usual position to indicate a pair of conjugated double bonds, such as ocimene has. The complex (triple) peak at about 278 mu. is characteristic in both position and shape for alloocimene (29).

Hydrogenation to Dihydromyrcene. The presence of ocimene was indicated by its reduction to dihydromyrcene (26) and by the preparation of the tetrabromodihydromyrcene (30).

The mixture of limonene and ocimene was dissolved in absolute alcohol and double the theoretical amount of sodium added, a gram at a time. The solution was allowed to boil. According to Semmler (30) limonene is not reduced under these conditions. After fractional distill-

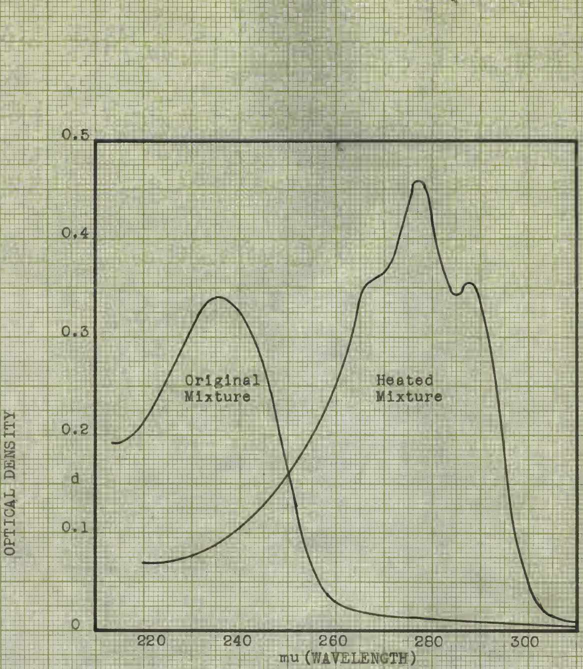


FIGURE 10

ULTRAVIOLET ABSORPTION OF OCIMENE-LIMONENE MIXTURE

Dilution in Iso-octane 1:200,000

ation the dihydromyrcene obtained boiled at 66 to 67° at 20 mm. as contrasted to the original boiling point of the mixture at 70-74°, and showed an index of refraction of 1.4505 at 25°. Semmler and Mayer (31) list the refractive index as 1.4507 at 20°. This indicates the possibility that the dihydromyrcene was about 90% pure. The dihydromyrcene was dissolved in ether, cooled in ice, and brominated by adding bromine dropwise with stirring. The ether was evaporated, and the viscous liquid dissolved in alcohol, decolorized with activated carbon, and recrystallized twice from cooled alcohol-water mixtures. The melting point was 82 to 85°. The pure tetrabromodihydromyrcene melts at 87-88° (30).

Summary

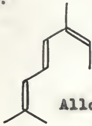
All the above evidence leads to the conclusion that ocimene is formed by isomerizing alpha pinene under the described conditions. It further demonstrates why other methods of thermally isomerizing alpha pinene yields allo-ocimene rather than ocimene.

CHAPTER V

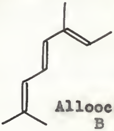
THE POLYMERIZATION OF ALLOCIMENE

Previous Work

Alloocimene, a readily available conjugated triene, was first reported by Enklaar in 1907 (26). He obtained it by refluxing ocimene. The ocimene had been obtained by the fractionation of natural oils at reduced pressure. Arbuzov described its production in the pyrolysis of alpha pinene in the vapor phase in 1933 (8,9), and Goldblatt and Palkin gave a very detailed description of the experimental procedure in 1941 (11). Fuguitt and Hawkins described its production from alpha pinene in the liquid phase in 1945 (13). In 1944 Hopfield, Hall, and Goldblatt (32) described two isomers of alloocimene. One, A, boils at 89° at 20 mm and freezes at -21°, while the other, B, boils at 91° and freezes at -34°. These are probably cis and trans isomers and are believed to be as shown below:



Alloocimene
A



Alloocimene
B

Goldblatt and Palkin also showed that in the vapor phase at 400° good yields of alpha and beta pyronene were obtained from alloocimene (12).

It had been shown previously by Fuguitt and Hawkins (13,16) that alloocimene in the liquid phase forms a dimer at a measurable rate at 180° or above. It was also shown that the reaction did not go to completion. Purified dimer, similarly, was shown to decompose to form about 12% monomer at 204.5°. It was also noted that the equilibrium mixture occupied about 10% less volume than the original alloocimene.

A preliminary calculation of the above rate constants for the reaction

$$2 \text{ alloocimene} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} \text{Dimer}$$

was made by Fuguitt (16) from data obtained at 189.5° and 204.5° by using a form of the equation developed by Walker and Appleyard, (33), but one in which no change in volume was considered. From the values of these constants the activation energy was obtained. The value of log s in the equation

$$\log k = \log s - E/2.3\,RT.$$

was obtained as illustrated for beta pinene in Appendix II. This gave a log s (in minutes) value for both the forward and reverse reaction between 10 and 11. As Fuguitt observed, this value is of the order of magnitude to be expected for a second order reaction rather than a first order one. As will be shown later, it makes little difference whether k_4 is calculated on the basis of a first or second order reverse process.

Density of Alloocimene-Dimer Mixtures

The large volume change in the mixture during the formation of a dimer appeared to make it important to know the relation between composition of the mixture and the density. This relation was determined, and is included in Table 14, page 58, and in Figure 11, page 59. The density of the mixtures, at the temperatures used by Fuguitt and in this work, are linear functions of the weight percent of the two components.

Effect of Addition of Acid, Base, and Antioxidant

Fuguitt's work (16) with alloocimene shows the formation of dimer to be a second order process. It has been postulated by Fuguitt and Hawkins (13) that this dimer is produced principally by a Diels-Alder reaction. To determine whether or not this reaction is influenced by the presence of mild acids, bases, or antioxidants, reagents of these types were added and rate measurements made. The reaction was carried out for several time

TABLE 14

Density of Alloocimene-Dimer Mixtures

Ampoule Number	Temp.	% Dimer	Expt. Density g/ml	Calculated Density (Interpolated)
H 93-1	204.5°	100.0	0.755	---
3	204.5°	74.5	0.731	0.731
5	204.5°	45.2	0.704	0.703
7	204.5o	25.0	0.684	0.684
9	204.5°	0.0	0.660	---

at 204.5° $d = 0.660 + 0.095$ (% Dimer)

2	189.5°	100.0	0.769	---
4	189.5°	74.5	0.742	0.744
6	189.5°	45.2	0.715	0.715
8	189.5°	25.0	0.695	0.695
10	189.5°	0.0	0.670	---

at 189.5°, $d = 0.670 + 0.099$ (% Dimer)

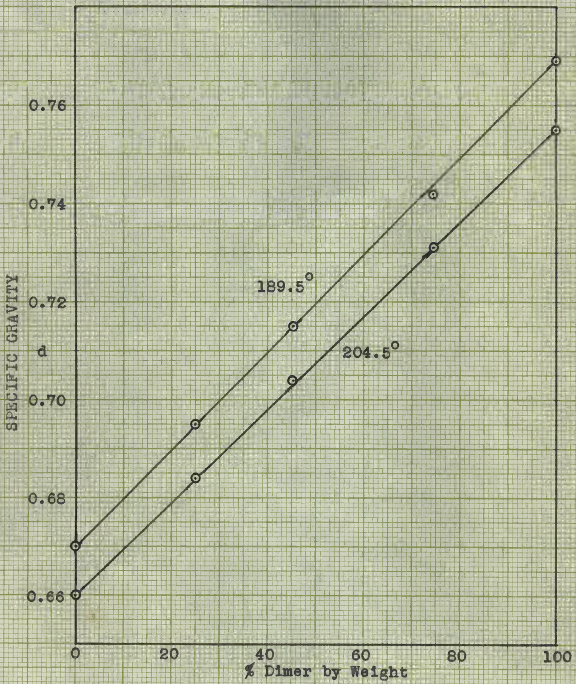


FIGURE 11. DENSITY OF ALLOOCIMENE-DIMER MIXTURES

intervals using different alloocimene samples to which were added 1% of benzoic acid, hydroquinone, or quinoline. Calculations were made on the basis of a first order reverse reaction in order to compare the value of k_4 with the value obtained by Fuguitt. Comparative data and results appear in Table 15, page 61. The conclusion is that the proton donors and acceptor did not significantly influence the reaction. Hydroquinone, in addition to being a weak acid, is an antioxidant. Since it did not affect the rate constant, it is believed that traces of oxygen are not taking part in a chain reaction.

Effect of Dilution

Fuguitt reported (16) a density of 0.740 g/ml for the equilibrium mixture obtained with alloocimene at 204.5°, in which there was 88% by weight dimer and 12% by weight alloocimene. A liter of this mixture was produced from 740/136 = 5.44 moles of alloocimene, and at equilibrium contained dimer from 5.44 x 0.88 = 4.79 moles of alloocimene.

For the reaction

$$2 \text{ alloocimene} \xrightleftharpoons[k_5]{k_4} \text{Dimer}$$

where a is the original number of moles per liter of alloocimene and x is the moles/liter alloocimene converted

TABLE 15

EFFECT OF ACID, BASE, AND ANTIOXIDANT ON THE POLYMERIZATION OF ALLOOCIMENE AT 204.5°

Expt. No.	t (min)	% Dimer Formed	k_4 $\frac{\text{liter}}{\text{mole min.}}$
1% Benzoic Acid Added			
			$\times 10^4$
H 132	32	28.0	25
H 133	75	43.1	21
H 134	152	58.0	19
H 135	312	66.3	17
1% Quinoline Added			
H 136	32	25.2	22
H 137	75	41.7	20
H 138	152	55.3	17
H 139	312	69.9	16
1% Hydroquinone Added			
H 140	32	26.8	24
H 15	72	42.2	21
H 14	182	64.9	22
Fuguitt (16) Average			22

at time $\underline{t}$, the rate of formation of dimer is $k_4\ (a-x)^2$, and the rate of decomposition of the dimer is $k_5\ x/2$

so $$\frac{dx}{dt} = k_4\ (a-x)^2 - k_5\ \frac{x}{2}$$

at equilibrium $\frac{dx}{dt} = 0$, and $x = x_e$

Hence $$k_4\ (a-x_e)^2 = k_5\ \frac{x_e}{2}$$

Substituting the above numerical values for $\underline{a}$ and $\underline{x_e}$

$$k_4 = (5.44 - 4.79)^2 = k_5\ \frac{4.79}{2}$$

$$\frac{k_4}{k_5} = \frac{x_e/2}{(a-x_e)^2} = 5.66$$

It has been shown (13) that no reaction takes place between alloocimene and dipentene. Hence dilution experiments using dipentene to alter the initial value of $\underline{a}$ are not complicated by interaction of alloocimene with dipentene. For the addition of two volumes of dipentene to one of alloocimene

$$a = \frac{5.44}{3} = 1.81$$

and since $$\frac{x_e/2}{(a-x_e)^2} = 5.66$$

the new value of $\underline{x_e}$ = 0.56 moles/liter. (The other root of this equation has a value of 5.83. This of course is meaningless here). The 0.56 m/l is 31% of the new value of a which is 1.81. Thus if the above relations represent the facts it should be expected that solutions of one mole of alloocimene in two moles of dipentene would approach an equilibrium mixture in which 31% of the alloocimene has formed dimer.

However, experiment showed that dilution did not change the proportion of alloocimene to dimer at the equilibrium point from that obtained in the absence of the diluent. This situation prevails if the reverse reaction is of the same order as the forward reaction. Hence the reverse reaction must be second order. This conclusion is in agreement with the implication, pointed out by Fuguitt (16), that a value of log s of about 10 applies to a second order equation.

Thus for the case where both reactions are second order the kinetic equation becomes

$$\frac{dx}{dt} = k_4\ (a-x)^2 - k_5\ \left(\frac{x}{2}\right)^2$$

at equilibrium $k_4\ (a-x_e)^2 = k_5\ \left(\frac{x_e}{2}\right)^2$

For undiluted alloocimene

$$\frac{k_4}{k_5} = \left(\frac{x_e/2}{a_e-x_e}\right)^2 = \left(\frac{4.79/2}{5.44-4.79}\right)^2 = 13.6$$

Change of concentrations due to dilution has no effect on the ratio of alloocimene to dimer at the equilibrium point. This can be shown by solving the last equation for $\underline{x_e}$ where the value of $\underline{a}$ is now 1.81 due to dilution

$$\left\{\frac{x_e/2}{1.81-x_e}\right\}^2 = 13.6$$

$$x_e = 1.59$$

$$1.59/1.81 = 88\%\ \text{dimer}$$

This is the same percent dimer found by experiment when no diluent is added. See page 60.

The experimental work used mixtures containing one mole of alloocimene diluted with two moles of dipentene. Samples were held at 204.5° for varying periods, as shown in Table 16, page 65. Also dimer was mixed with twice its weight of dipentene and this mixture also held at 204.5° for various lengths of time. The table shows that the equilibrium point is approximately 89% dimer.

The conversion of dimer to alloocimene appears to be an example of a monomolecular reaction in the liquid phase which follows a second order rate equation.

Methods of Treating Data

Fuguitt's data for the polymerization of alloocimene are listed in Table 17, page 66, and Table 18,

TABLE 16

ALLOOCIMENE POLYMERIZATION AT 204.5°

One Part Alloocimene in Two Parts Dipentene

Expt. No.	Time (min)	% Dimer Recovered	k_4 $\frac{\text{Liters}}{\text{Moles min.}}$
H 110	124	23.9	16×10^{-4}
H 111	235	42.2	20
H 176	730	64.2	17
H 175	1620	75.2	---
H 177	3550	81.8	---
H 178	4290	83.4	---
H 186	12400	89.2	---

One Part Dimer in Two Parts Dipentene

H 173	2856	89.5
H 174	4300	89.0
H 189	8780	90.6
H 188	12400	93.1

TABLE 17

THE REVERSIBLE DIMERIZATION OF ALLOOCIMENE AT 189.5°

At Equilibrium there is 89% by Weight Dimer

First Order Reversible Reaction By Fuguitt (16)				First Order Reversible Reaction, Volume Corrected	Second Order Reversible Reaction	
					Volume Corrected	Mole Fraction
Tube	t min.	% Dimer	k_4 $\frac{\text{liter}}{\text{mol.min.}}$ x 10^4	k_4 $\frac{\text{liter}}{\text{mol.min.}}$ x 10^4	k_4 $\frac{\text{liter}}{\text{mol.min.}}$ x 10^4	k_4 $\frac{1}{\text{min.}}$ x 10^4
50	108	34	9.1	9.9	9.5	23.8
51	108	32	7.9	8.9	8.8	21.8
52	254	54	8.5	9.5	9.4	23.2
53	254	53	8.3	9.1	9.0	22.3
54	408	64	8.1	9.0	8.9	22.2
55	408	65	8.5	9.5	9.3	23.2
56	720	76	8.7	9.5	(9.2)	(23.2)
57	720	76	8.7	9.5	(9.2)	(23.2)
58	1020	80	7.8	8.9	(8.5)	(21.5)
60	1440	84	8.1	8.9	(8.5)	(21.6)
61	1440	85	8.9	9.8	(9.4)	(24.3)

Use averages from 33 to 67% Dimer only

	Volume Corrected	Mole Fraction
Average	9.15	22.8
Average Deviation	2.7%	2.8%

TABLE 18

THE REVERSIBLE DIMERIZATION OF ALLOOCIMENE AT 204.5°

At Equilibrium there is 88% by Weight Dimer

First Order Reversible Reaction By Fuguitt (16)				First Order Reversible Reaction, Volume Corrected	Second Order Reversible Reaction	
					Volume Corrected	Mole Fraction
Tube	t min.	% Dimer	k_4 $\frac{\text{liter}}{\text{mol.min.}}$ $\times 10^4$	k_4 $\frac{\text{liter}}{\text{mol.min.}}$ $\times 10^4$	k_4 $\frac{\text{liter}}{\text{mol.min.}}$ $\times 10^4$	k_4 $\frac{1}{\text{min.}}$ $\times 10^4$
68	50	32	23	20	20	47
69	50	33	24	21	21	49
70	130	54	22	19	19	45
71	130	54	22	19	19	45
72	185	65	26	22	21	51
73	185	63	23	20	19	47
74	285	71	22	19	(18)	(44)
75	285	70	21	19	(18)	(43)
76	395	75	20	18	(17)	(40)
77	395	75	20	18	(17)	(40)
78	640	81	19	16	(16)	(38)
79	640	81	19	16	(16)	(38)

Use averages from 33 to 66% Dimer

Average	19.8	47.3
Average Deviation	4.2%	3.7%

page 67, together with the values of k_4 which he obtained on the basis that the reverse reaction was first order and that the volume change was negligible. In the same table are listed the results of treating the data by other methods.

Mole Fractions. A method to avoid the change in volume factor is to use mole fractions as the concentration unit.

Let N = the mole fraction of dimer

and 1-N = the mole fraction of alloocimene

then
$$\frac{dN}{dt} = k_4\,(1-N)^2 - k_5\,N^2$$

at equilibrium
$$k_4\,(1 - N_e)^2 = k_5\,N_e^2$$

$$k_5 = k_4\,\frac{(1-N_e)^2}{N_e^2}$$

Using data from Table 18, page 67, for the equilibrium mixture at 204.5°

$$N_e = \frac{88/2}{12 + 88/2} = 0.786$$

Hence
$$k_5 = 0.0742\,k_4$$

Substituting for k_5 in the above rate equation

$$\frac{dN}{dt} = k_4\,(1-N)^2 - 0.0742\,k_4\,N^2$$

and $k_4\ dt = \dfrac{dN}{1-2\ N+N^2-0.0742N^2} = \dfrac{dN}{1-2\ N+0.9258N^2}$

Integration and conversion to $\log_{10}$ gives

$$k_4 = \frac{4.22}{t} \log \frac{1.375 - N}{0.786 - N} + C.$$

When $t = 0$, $N = 0$, and $C = -4.22 \log \dfrac{1.375}{0.786}$

Hence $\quad k_4 = \dfrac{4.22}{t} \log 0.571 \dfrac{1.375 - N}{0.786 - N}$

Similarly, at 189.5°

$$k_4 = \frac{4.66}{t} \log 0.604 \frac{1.328 - N}{0.802 - N}$$

The values calculated by this method appear in column 7, Table 17, page 66, and Table 18, page 67.

Moles per Liter Rate Constants (on Basis of Second Order Reverse Reaction). In writing the differential equation to express the rate of dimerization of alloocimene with time, according to the reactions

$$2 \text{ alloocimene} \underset{k_5}{\overset{k_4}{\rightleftarrows}} \text{Dimer}$$

$$\frac{dx}{dt} = k_4\ (a-x)^2 - k_5 \left(\frac{x}{2}\right)^2$$

where a is the original concentration of alloocimene in moles per liter, and x is the amount reacted at time t.

At equilibrium $dx/dt = 0$, $x = x_e$, $a = a_e$ and

$$k_4 \, (a_e - x_e)^2 = k_5 \, (x_e/2)^2$$

$$k_5 = \left(\frac{a_e - x_e}{x_e/2}\right)^2 k_4$$

The difference between $\underline{a_o}$ and $\underline{a_e}$ is proportional to the difference between the density of pure alloocimene and the density of the equilibrium mixture.

Hence
$$\frac{dx}{dt} = k_4 \, (a-x)^2 - k_4 \left(\frac{a_e - x_e}{x_e/2}\right)^2 \left(\frac{x}{2}\right)^2 .$$

As $\underline{t}$ and $\underline{x}$ change, the density of the reaction mixture increases, or the volume decreases, and hence the value of $\underline{a}$ changes with $\underline{t}$ and $\underline{x}$. A correction for this change in $\underline{a}$ can be made by expressing $\underline{a}$ as a function of $\underline{x}$. The densities of the mixtures in terms of weight percent of dimer are given in Table 14, page 58. From these relations the corrected values of $\underline{a}$ in terms of the corresponding value of $\underline{x}$ can be calculated for any time $\underline{t}$. This is readily done as illustrated for tube 68 of Table 18, page 67. The equation for a straight line representing densities vs weight fraction at 204.5° in Figure 11, page 59 is

$$d = 0.660 + 0.095 \text{ (weight fraction dimer).}$$

$$d = 0.660 + 0.095 \; (0.32) = 0.6904$$

$$a = \frac{1000 \times 0.6904}{136} = 5.077 \text{ moles/liter}$$

The amount of alloocimene reacted, x, is equal to the value of a, corrected for the change in density, times the weight fraction of alloocimene that has been converted to dimer. In the illustration chosen

$$x = 5.077 \times 0.32 = 1.625 \text{ moles/liter.}$$

A series of values of a and x were obtained in this manner, and were plotted in Figure 12, page 72. It is obvious that this is not exactly a straight line relation. However, in view of the fact that the relation is almost linear, it was treated as such in order to simplify the calculation. It should be kept in mind that any error due to this simplification is one of second order in view of the fact it involves a small error in the equation used to express the relation between x and the change in density. The equation for the straight line in Figure 12, page 72, is

$$a = 4.85 + 0.132\ x.$$

When substituted into the rate equation, it gives

$$\frac{dx}{dt} = k_4\ (4.85+0.132\ x-x)^2 - k_4 \left(\frac{a_e-x_e}{x_e/2}\right)^2 \left(\frac{x}{2}\right)^2.$$

Evaluation of a_e and x_e from the fact that 88% of the alloocimene is converted to dimer at equilibrium at 204.5° gives values of

$$a_e = 5.453 \text{ and } x_e = 0.88 \times 5.453.$$

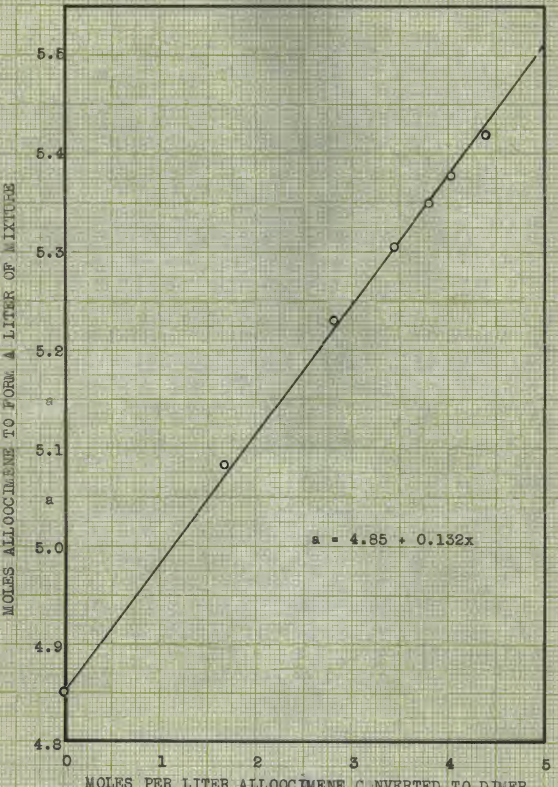


FIGURE 12. VOLUME CORRECTION FOR ALLOOCIMENE REACTION

Thus $\frac{dx}{dt} = k_4 (4.85 - 0.868x)^2 - 0.0186\ k_4x^2$

or $k_4\ dt = \frac{dx}{23.522 - 8.4196\ x + 0.7348\ x^2}.$

Integrating and converting to log to the base 10

$$k_4t = 1.74 \log \frac{6.63 - x}{4.83 - x} + C.$$

Evaluating the integration constant when t = 0, x = 0,

$$C = -1.74 \log \frac{6.63}{4.83} = 1.74 \log 0.729$$

and $k_4 = \frac{1.74}{t} \log 0.729 \frac{6.63 - x}{4.83 - x}.$

Substituting the values of $x = 1.625$ and $t = 50$ min.

$$k_4 = 0.0020.$$

Similarly for 189.5° $a_e = 5.574$, $x_e = 0.89 \times 5.574$

and $k_4t = 1.888 \log 0.750 \frac{6.65 - x}{4.99 - x}.$

The values of k_4 obtained with these equations also appear in Table 17, page 66, and Table 18, page 67.

Moles per Liter Rate Constants (on Basis of First Order Reverse Reaction). The preliminary calculation for k_4 and k_5 made by Fuguitt assumed a first order decomposition of dimer to form monomer. Using the method of correction for volume change developed above with the differential equation for the reaction

$$2 \text{ Alloocimene} \rightleftharpoons \text{Dimer}$$

$$\frac{dx}{dt} = k_4 \, (a - x)^2 - k_5 \, \frac{x}{2}.$$

Substituting for k_5 in terms of k_4 (page 69)

$$\frac{dx}{dt} = k_4 \left\{ (a-x)^2 - \frac{(a_e - x_e)^2}{x_e/2} \, \frac{x}{2} \right\}.$$

Substituting $a = 4.85 + 0.132 \, x$ again, and the values $a_e = 5.453$ and $x_e = 0.88 \times 5.453$, and simplifying

$$k_4 \, dt = \frac{dx}{23.56 - 8.515 + 0.753 \, x^2}.$$

Thus $$k_4 = \frac{1.87}{t} \log 0.748 \, \frac{6.47 - x}{4.83 - x}.$$

The values of k_4 obtained by use of this equation are shown in column 5, Table 17, page 66, and Table 18, page 67.

Comparison with the next column demonstrates how little difference in k_4 results when the reverse reaction is considered to be first or second order.

The values of k_5 are appreciably different when the reverse reaction is treated as second order rather than first order. However, in each case k_5 is small compared to k_4 and hence the value of k_4 is not appreciably affected by the two different treatments of the reverse reaction.

Weight Fractions. The density of the reaction mixture was found to be a linear function of the weight fraction of the dimer present, as shown in Figure 11, page 59. Consequently the value of a is a linear function of the weight fraction, resulting in an exact form of differential equation that can be integrated readily. Evaluating x in terms of a and the weight fraction of dimer, w,

$$x = aw$$

and $$\frac{dx}{dt} = a\,\frac{dw}{dt}.$$

Substituting these in

$$\frac{dx}{dt} = k_4\ (a-x)^2 - k_4 \left\{\frac{a_e - x_e}{x_e/2}\right\}^2 \left\{\frac{x}{2}\right\}^2$$

then $$\frac{dw}{dt} = k_4\ a \left[\ (1-w)^2 - \left\{\frac{1-w_e}{w_e}\right\}^2 w^2 \right].$$

Introducing the volume correction

$$a = a_o + bw$$

and simplifying

$$k_4\ dt = \frac{dw}{(a_o + bw)\ (1-2w+fw^2)}$$

where $$f = 1 - \left(\frac{1-w_e}{w_e}\right)^2.$$

This form of differential equation appears in a table of integrals (33) and when used with the same data as was used for the sample calculation involving moles per liter units, which appears on page 70, yields

$$k_4 = \frac{0.0265}{t} \log \frac{(1+0.439w)^2}{1-2w+0.9814w^2} + 57.3 \log 0.758 \frac{1.16-w}{0.88-w}.$$

Data from Table 18, page 67, for tubes 68 and 79 give values of k_4 of 18×10^{-4} and 15×10^{-4} respectively. The previous method using an approximate volume correction gives 20×10^{-4} and 16×10^{-4} respectively.

The above calculations of the data for this reaction also result in values for k_4 which decrease somewhat as the reaction proceeds. It is believed that there may be other reactions occurring, to a limited extent, which are not taken into account in the rate equation.

The weight fraction unit equation is of some interest in that it can be derived from the mole fraction equation to show the relationship between the numerical size of the constants for each. Thus

$$N = \frac{w/2}{\frac{w}{2} + (1-w)} = \frac{w}{2-w}$$

$$\frac{dN}{dt} = \frac{2}{(2-w)^2}\frac{dw}{dt}$$

Substituting these into

$$\frac{dN}{dt} = k\ (1-N)^2 - \left\{\frac{1-N_e}{N_e^2}\right\} kN^2$$

it develops that

$$\frac{dw}{dt} = 2\ k\ \left[(1-w)^2 - \left\{\frac{1-w_e}{w_e}\right\}^2 w^2 \right].$$

Comparison with

$$\frac{dw}{dt} = k_4 a\ \left[(1-w)^2 - \left\{\frac{1-w_e}{w_e}\right\}^2 w^2 \right]$$

shows that $2k = k_4 a$

and $k = \frac{a}{2} k_4$.

This demonstrates that the use of mole fractions in such a reaction does not correct for volume changes, since k_4 as set up above has had no correction for volume change applied to it.

Calculation of Constants on the Basis of a Second Order Reverse Reaction and Correction for the Volume Change.

Moles per Liter. The values of k_4 from Table 17, page 66, and Table 18, page 67, can be used with the equilibrium mixture composition to determine the values for k_5 which is the velocity constant for the decomposition of the dimer in a second order reaction.

At equilibrium $k_4\ (a_e-x_e)^2 = k_5 \left\{\frac{x_e}{2}\right\}^2$.

At 189.5°, $x_e = 0.89\ a_e$, $k_4 = 0.000915$ l/mole min.

$$k_5 = k_4 \frac{4(1-0.89)^2}{(0.89)^2} = 5.60 \times 10^{-5} \text{ liter/mole min.}$$

at 204.5°, $x_e = 0.88\ a_e$, $k_4 = 0.00198$ l/mole min.

$$k_5 = k_4 \frac{4(1-0.88)^2}{(0.88)^2} = 14.7 \times 10^{-5} \text{ l/mole min.}$$

The energy of activation E, for both the formation of the dimer and for its decomposition were calculated using the Arrhenius equation in the form

$$\log \frac{k_2}{k_1} = \frac{E\ (T_2-T_1)}{2.3R\ T_1T_2}$$

Substituting the values of E thus obtained in the other form of the same equation,

$$\log s = \frac{E}{2.3RT} + \log k,$$

the value of the collision number for the two reactions were calculated. The values of these constants are shown in Table 19, page 79, and indicate that both reactions are probably second order. It must be noted that log s is in terms of seconds, instead of minutes.

The conventional equilibrium constant for the reaction

TABLE 19

SUMMARY OF CONSTANTS FOR ALLOOCIMENE DIMERIZATION

Temp.	Constant	Reaction	
		2 Alloocimene $\longrightarrow$ Dimer	Dimer $\longrightarrow$ 2 Alloocimene
Using Moles per Liter Units			
189.5°	k(liter/mole min.)	9.15×10^{-4}	5.6×10^{-5}
189.5°	K	16.4	---
204.5°	k(liter/mole min.)	19.8×10^{-4}	14.7×10^{-5}
204.5°	K	13.4	---
---	$E_{act.}$(calories/mole)	22,600	28,300
---	ΔH (calories/mole)	-5,800	---
---	log s (using seconds^{-1})	5.9	7.3
Using Mole Fraction Units			
189.5°	k (min.$^{-1}$)	22.8×10^{-4}	13.9×10^{-5}
189.5°	K	16.4	---
204.5°	k (min.$^{-1}$)	47.3×10^{-4}	35.2×10^{-5}
204.5°	K	13.4	---
---	$E_{act.}$(calories/mole)	21,200	27,200
---	ΔH (calories/mole)	-5,800	---

$$2 \text{ alloocimene} \rightleftharpoons \text{Dimer}$$

is $$K = \frac{(C_{dimer})}{(C_{alloocimene})^2} = \frac{x_e/2}{(a_e - x_e)^2}.$$

The values of K obtained thus were used in the Van't Hoff Equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H \ (T_2 - T_1)}{2.3 \ R \ T_1 T_2}$$

to obtain a value for Δ H, the heat of reaction of the above reaction. At 189.5°, K was found to be 6.60, and at 204.5° it was 5.60. The corresponding value for the heat of reaction, Δ H, is -4800 calories per mole. This does not represent the difference between the heats of activation between the forward and reverse reactions.

The equilibrium constant is also defined, more logically, as the ratio of the forward and reverse reaction rates. In this case the reverse reaction is not first order as might be expected from inspection of the overall reaction, so the equilibrium constant must be

$$K = \left(\frac{C_{dimer}}{C_{alloocimene}}\right)^2 = \left(\frac{x_e/2}{a_e - x_e}\right)^2.$$

The values obtained using this equation are shown in Table 19, page 79. The heat of reaction obtained from these values of K is approximately equal to the difference between the heats of activation of the opposing reactions, as it should be.

Mole Fractions. In the rate equation using mole fractions, at equilibrium

$$k_4\ (1-N_e)^2 = k_5\ N_e^{\ 2}$$

at 189.5° $N_e = \frac{0.89}{2-0.89}$, and $k_4 = \frac{22.8 \times 10^{-4}}{\text{min.}}$

$$k_5 = 1.39 \times 10^{-4}/\text{min.}$$

at 204.5° $N_e = \frac{0.88}{2-0.88}$, and $k_4 = 47.3 \times 10^{-4}$

$$k_5 = 3.52 \times 10^{-4}/\text{min.}$$

The mole fraction equilibrium constants for the reaction

$$2\ \text{allocimene} \rightleftharpoons \text{Dimer}$$

are given by

$$K = \frac{(C_{\text{dimer}})^2}{(C_{\text{allocimene}})^2} = \frac{(N_e)^2}{(1-N_e)^2}$$

and are shown also in Table 19, page 79. From these values for K the heat of reaction was calculated. It must be noticed that the heats of activation as calculated from moles per liter units do not agree with those from mole fraction units. The discrepancy may depend on the fact that there is a change in volume which is not taken into consideration by the mole fraction expression for reaction rate constant calculations.

Dilatometeric Determination of Rate Constants

In an attempt to measure the progress of the reaction with greater procision, two experiments with dilatometers were made. One used alloocimene as the starting material, and the other used dimer. The bulb of the dilatometer was the same in each experiment. In the first experiment a large tubular neck was used to accomodate a 10% volume shrinkage while a second neck was made to take care of a 1% volume increase.

The results, shown in Table 20, pages 83 and 84 and Table 21, page 85, show the same drift of the reaction rate constant k_4 as was shown by the data determined by Fuguitt. The complete data are shown in the table, though calculations are made for only part of them. The data for the experiment using dimer as the starting material are included. It will be noted that the density of this sample of dimer is much higher than that used for the determination of the density of mixtures. This sample of dimer was obtained in dimerization reactions where the mixtures were heated several days as contrasted to several hours for the sample used for the densities of mixtures. Also, the equilibrium point seemed to be at about 7% alloocimene, instead of 11-12%. This indicates that reversible dimerization and the formation of pyronenes

TABLE 20

DIMERIZATION OF ALLOOCIMENE AT 204.5° IN DILATOMETER

Experiment H 92. Equilibrium Point 88% Converted.

At Start: 12.5 cm., 43.70 ml, d = 0.661, a = 4.86

At Equilibrium: 0 cm, 38.80 ml, d = 0.745, a = 5.47

Vol. = 38.80 + 0.392 cm, d = 28.9/vol, % = (d-0.661) 880/0.84

cm	t (min)	Vol. (ml)	d g/ml	% allo. used	x	k_4 $\frac{\text{liters}}{\text{moles min}}$
12.50	0					
12.28	1					
12.10	3					
11.81	5.5					
11.43	9	43.29	0.6675	6.8	0.33	17
10.80	15					
10.30	21	42.84	0.6746	14.3	0.71	17
9.69	30					
9.41	34	42.49	0.6802	20.1	1.01	16
9.02	40					
8.69	45	42.20	0.6848	25.0	1.26	15
8.23	53					
7.82	61					
7.32	72	41.67	0.6936	34.2	1.74	15
6.72	85					
6.30	98	41.26	0.7015	42.5	2.19	15
5.62	120					
5.00	145	40.74	0.7094	50.7	2.64	15
3.84	210					
3.50	232	40.17	0.7195	61.3	3.24	14

Table 20 Continued

cm	t (min)	Vol. (ml)	d g/ml	% allo. used	x	k_4 $\frac{\text{liters}}{\text{moles min}}$
2.95	288	39.96	0.7233	65.4	3.47	14
2.73	316					
2.49	352					
2.28	385					
2.12	412					
1.39	658	39.35	0.7344	76.9	4.15	(11)
1.16	670					
0.92	978					
0.80	1092					
0.74	1171	39.09	0.7393	82.0	4.45	(9)
0.69	1292					
0.63	1405					
0.50	1690	39.0	0.741	83.9	4.57	(8)
0.40	2431					
0.20	2851					
0.10	3250					
0.01	3886					

TABLE 21

REVERSIBLE DISSOCIATION OF DIMER TO ALLOOCIMENE AT 204.5°

Original density = 0.770, a = 2.83

Equilibrium density = 0.765 at 6.0 (?) cm.

At 2510 min, 6.7% alloocimene formed = 0.19 m/l alloocimene reacted.

Min.	Cm	x m/l
32	0.32	0.010
94	0.85	0.027
139	1.23	0.040
184	1.59	0.051
252	2.08	0.067
324	2.53	0.0815
770	4.62	0.149
1060	5.32	0.1715
1594	5.81	0.187
2510	5.90	0.190

may not be the only reactions taking place at this temperature.

APPENDIX I

LABORATORY PROCEDURES

Purification of Materials

Alpha and beta pinene were obtained as commercial products of approximately 95% purity through the courtesy of the Naval Stores Division of The Glidden Company, Jacksonville, Florida. These were purified in five liter batches by fractional distillation through rectification columns of the Lecky and Ewell type (35). The columns exerted more than 60 theoretical plates at total reflux. A total condensation type head with a simple magnetic take-off control was developed for this purpose (36). The column was operated at a reflux ratio of about 100 to 1. The pressure at the distilling head was maintained constant at 20 mm of mercury by a Hirschberg and Huntress type manostat (37). The alpha pinene was readily purified to a constant boiling point of 52° to 20 mm and a refractive index of $n_D^{25} = 1.4631$. The beta pinene was distilled using a reflux ratio of 100-150 to 1 and showed a constant boiling point of 60° at 20 mm and a refractive index of $n_D^{25} = 1.4763$-4. Previous work in this laboratory (38) showed that carefully purified beta pinene had a refractive index of 1.4768 under the same conditions. A sample of carefully purified beta pinene prepared by The Glidden Company laboratory showed the same index of refraction as the sample purified for this work.

Some alloocimene was obtained as a 90% pure material from The Glidden Company, and some was made in this laboratory from alpha pinene according to the method of Goldblatt and Palkin (11). The procedure is to carry the purified alpha pinene in a stream of nitrogen through a tube maintained at 450° and condense out the products. Fractionation of the products yielded 30% alloocimene which had a refractive index of n_D^{25} = 1.5425, and boiled at from 89 to 91° at 20 mm. This compares favorably with the values reported by Goldblatt and Palkin (11). The other products of this isomerization have boiling points below 72° or above 140° at this presure, so a good separation was readily obtained. The refractive index of any of the products boiling below 72° is less than n_D^{25} = 1.489, so the purity of this material should be quite good, probably above 99%. The two forms of alloocimene (32) boil two degrees apart, but as the present investigation was undertaken to extend the work of Fuguitt, who used the mixture of isomers obtained from alpha pinene, the same mixture was likewise used in these experiments.

Dipentene (dl-limonene) was obtained from the pyrolysis of alpha pinene at the same time as alloocimene, and was purified by rectification through a Lecky and Ewell type column capable of exerting thirty theoretical plates at total reflux. The reflux ratio used was 7 to 1. The finished product had a boiling range of less than 0.1° and a refractive index of $n_D^{25} = 1.4701$. The boiling point was 71° at 20 mm.

All terpenes were stored under nitrogen or under a vacuum. This precaution was found to be very important, especially with alloocimene and ocimene.

Quinoline, hydroquinone, and benzoic acid were the best grades commercially available, and the quinoline was redistilled.

Sealed Reaction Ampoules

Pyrex Brand medium wall laboratory tubing of about 38 mm outside diameter, with 3 mm wall thickness, was made into ampoules. It was drawn down to about 8 mm o.d. and a six inch length of 8 mm tubing sealed on. The other end of the ampoule was sealed off in a rounded shape similar to that of the bottom of a test tube. The wall thickness was kept fairly heavy, (approximately 3 mm) bearing in mind that the small neck needed less thickness than the larger body of the ampoule. Each ampoule was annealed after it was made and after each new neck was sealed on. In this laboratory a group of three Tirrill or two Fisher burners did very well in relieving strains, without appreciable distortion of the constantly turned ampoule. Each ampoule was inspected for strains between crossed Polaroid films, and those with serious strains were reannealed.

Ampoules were cleaned by blowing a slow stream of air into them, by means of a 5 mm hard glass tube thrust down the neck, during the annealing process. This method avoided the use of cleaning solutions which ordinarily are completely removed only with difficulty. After opening, the ampoules were rinsed with ether and drained. In the sealing process in which a new neck was added there was some carbonization as well as oxidation. During the annealing and cleaning process all this organic material was burned out and the products of combustion carried away by the air stream.

The ampoules were filled with nitrogen by blowing out the air. Liquids were then introduced into the necks of the upright ampoules with volumetric pipettes. Solids were dropped down a small thistle tube made of 5 mm tubing, which was long enough to extend into the body of the ampoule. The fluffy, needle-like crystals of benzoic acid were reduced to a free flowing form by pulverizing the compact solid left after the benzoic acid was melted and allowed to freeze. The maximum thermal expansion of the liquids was of the order of twenty five percent, so no ampoules were filled more than two thirds full at room temperature. The necks of the ampoules were cleaned with pipe cleaners or similar devices, although with the readily volatile nature of the materials used, this was not essential.

The ampoules were evacuated before sealing to minimize oxygen contamination of the mixture and to lower the pressure in the glass ampoule at the reaction temperature. Heavy walled rubber tubing was used to connect the ampoule to a manometer, cold traps, and vacuum pump. The pressure was reduced to 1 mm in the system, and a stopcock used to cut off the manometer and ampoule from the traps and pump. The ampoule was shaken very gently at first and then briskly, taking care that foaming and splashing did not cause loss of material into the rubber tubing. During the first few seconds of shaking, considerable gas was given off, resulting in violent foaming. After a minute or so of shaking the pressure rose to 10 or 20 mm and remained constant. Shaking was discontinued while the system was evacuated to 1 mm again and the pump again cut off. By shaking the liquid in the ampoule only when the system was cut off from the pump it was found that good removal of gas from the liquid was possible with very small loss of terpene. The ampoule was then clamped in a slanting position and the neck heated with a Tirrill burner, gently at first over a several inch range to distill away any materials in the neck, then very strongly on first one side, then the other, until the neck flattened together. It was then drawn out somewhat and melted apart.

Ordinary gummed labels were used for marking the tubes, with the numbers retraced several times with a pen to scar the paper surface.

Ampoules were wired into metal holders of sufficient weight to maintain position in the oil bath. They were hung completely immersed in the oil, well away from the heated walls, knife heaters and the stirrer.

The Oil Bath

The cylindrical container was 12 inches in diameter and 13 inches high, and held five gallons of oil. It was large enough to hold seven of the ampoules at one time. The entire cylindrical wall of the bath below the oil level was wound with heating coils capable of

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cooling?

maintaining the temperature of the bath about fifteen degrees below the temperature desired. The bath was insulated with four inches of asbestos at the bottom and sides. A knife heater, using 125 watts when operating and activated by a relay, was used to keep the temperature at the desired point. The thermoregulator to control the relay had a mercury filled bulb of 14 mm Pyrex tubing six inches long, connected to a contact neck made of .25 mm capillary tubing. Since operating temperatures ranged up to 235°, the contact in the capillary tube could not be made at a point near the bulb, because mercury was found to distill up the empty capillary. By using an elongated capillary, and making contact between platinum wire and mercury well above the oil level at a point where the temperature was about 40°, satisfactory operation was obtained. A two stage commercial relay was used. To prevent oxidation of the mercury surface at the contact point with the platinum, a nitrogen atmosphere was found satisfactory. Control was obtained to 0.1°, and thermometers standardized by the U. S. Bureau of Standards were used to set the thermoregulator.

A suitable oil was U. S. P. Extra Heavy Mineral Oil, or Liquid Petrolatum, commonly used as a laxative. Different samples of this behaved differently, but were useable up to 235° without signs of approaching the flash point as the oil aged. At 200° the oil thickened and formed a small amount of gummy material, but at 235° it was quite fluid and at the same time developed a fine black precipitate that did not coagulate or become attached to the container. The vapor pressure of the oil was such that everything near the bath was wetted with oil. At no time was the flash point reached. This point was as low as about 275° for some samples tested. Because of the tendency to distill, improvement would result if the lid were fitted down into the top of the bath, allowing condensate to drop into the liquid instead of running over the edge into the insulation. Similarly the bath should be constructed in such a manner as to prevent accidental dropping of oil into the insulation during removal of ampoules. The continual loss of oil made it necessary to add oil occasionally during treatment of samples. This was done by adding oil drop by drop from a large dropping funnel, or by heating oil to about five degrees above the required temperature and pouring it in. Either method was satisfactory and did not disturb the temperature of the bath appreciably.

When an ampoule was introduced into the bath the temperature dropped more than a degree. To offset this, extra knife heaters were used to bring the temperature back to the operating point quickly. By using 500 watts of extra heat several ampoules could be introduced at the same time with little disturbance of the average temperature of the oil.

A large and efficient stirrer was used to keep the temperature uniform throughout the bath. The part of the bath occupied by the ampoules varied less than 0.1° at various points.

Hydrogenated cottonseed oil was used for some of the early work, but it was less satisfactory than mineral oil because it became very thick and viscous, which made uniform temperature difficult to obtain. Also, as the oil aged its initially high flash point decreased.

Analytical Distillation of Alloocimene-Dimer Mixtures

The separation of the dimers of alloocimene from the alloocimene does not require a very efficient column. Alloocimene boiled at 88° and the dimers at about 160° at 20 mm.

Each ampoule was opened by scratching a mark on the neck with a file and applying the melted end of a stirring rod to one end of the mark. A crack developed which allowed easy removal of the neck. The sample was poured into a tared 200 ml round bottom flask, equipped with a thermometer well and an interchangeable female ground joint, and weighed again. The interchangeable joint was fitted on the male joint at the bottom of the distilling column and warmed until the sealing compound melted and formed a transparent, tight joint.

The sealing compound found most satisfactory was a mixture of polyhydroxy compounds insoluble in hydrocarbons (39). The original proportions were found to contain too much glycerine and to form too thin a gel. This showed tendencies to be pushed into the system by the pressure difference of nearly an atmosphere, and produced leaks. By using much less glycerine, a stiffer gel formed, and to get good joints the material had to be melted. In taking a joint apart the sealing compound was melted by heating the female joint with the hot blue cone of the flame of a Tirrell burner. This melted the compound around the female joint surface, and separation of the joint left any excess adhering to the male part. This resulted in a very uniform small amount of compound on the flasks used, and gave constant tare weights. Too much heating before a joint was separated caused carbonization of the sealing compound, and then the female part had to be broken to remove the flask from the distilling column. Terpenes and the solvents used to clean the apparatus, such as ether and tetrochlorethane, did not remove the sealing compound, though alcohols or water did so readily.

The distilling column was a glass tube about 10 mm in diameter with a six inch length of packing. It had a thermometer inserted at the top and a side arm with a condenser attached. The packing was a strip of stainless steel gauze, 50 x 50 wires per inch, that would just slip into the glass tube, twisted 90° every quarter inch (40). The column was insulated with a layer of aluminum foil, a half inch of fluffy glass wool, and another layer of aluminum foil. No electrical heater was required for this column.

The distillation was carried out at 20 mm. pressure. The system was controlled by a Hirschberg-Huntress manostat, using trimethylene glycol with a drop of sulfuric acid in it instead of sulfuric acid. !?

The distillation pot was first heated by a mantle heater, and the top of the pot was insulated. It was discovered that mixtures containing alloocimene and its polymers were particularly prone to superheat and to bump so vigorously as to blow large quantities of material from the pot into the receivers. Ebulator tubes are not desirable in quantitative work on easily oxidized terpenes, and internal bare wire heaters are not convenient for very small residues. The distillations were almost all carried out under conditions of continuous, controlled bumping using a small flame from a Tirrill burner directed by hand at the side of the flask just below the liquid level. This was satisfactory, though time consuming.

The distillation was carried out slowly, and the temperature in the pot reached the boiling point of the dimer before the temperature in the head passed 90°, which is the boiling point of the higher boiling form of alloocimene. The distillation was stopped when the thermometer in the distilling head showed, by the sudden increase in temperature, that the dimers had reached the bottom of the thermometer, which was an inch below the sidearm. After a half hour under vacuum, to allow for cooling and for draining of the column, both pot and receiver were weighed. Usually the sum of the residue and distillate weights equalled the pot sample weight within one percent.

Analytical Distillation of the Products from the Pinenes

The analytical distillation of the mixtures of products obtained from the thermal isomerization of the pinenes requires efficient fractionating columns. Prior work (15) has indicated that Lecky and Ewell type columns (28) are very satisfactory. However, in this work a Bower and Cooke type column was used (40). The columns were 7 and 10 mm o.d. and four feet long. The packing was made from strips of stainless steel gauze that would just slip into the columns. This metal ribbon was twisted 90° every quarter inch, and pulled into the tube. The non-drainable holdup in these columns was from 0.2 to 0.4 g. Such a small column was best operated in a large jacket which was electrically heated. Fluffy glass wool filled the space between the column and the jacket. This prevented convection currents inside the jacket itself, and the insulating properties of the glass wool allowed the vapors to maintain the walls of the column of few degrees above the temperature of the jacket. Since the bottom of the column was sometimes several degrees warmer than the top, this made adjustment of the jacket temperature much less difficult.

The distilling heads used on the columns were of total condensation types in which the takeoff rate was adjusted by setting a stopcock. The entire head from the condenser down to the heating jacket of the distilling column was wrapped in a "quilt" of glass wool between sheets of aluminum foil. This type of insulation is readily made, easily placed in position and removed, and is quite efficient.

The distillation pots were the same 200 ml flasks used for the distillation of alloocimene. They were heated by mantle heaters that covered not more than one third the height of the spherical part of the flask, and were built to fit the size flask used. A quilt of aluminum foil and glass wool extended from the bottom of the column heater to the top of the heating mantle.

The distillations were carried out somewhat differently from the method of Fuguitt (16). He collected many small fractions of distillate, and calculated the composition of each from the refractive index. Here it was found that satisfactory results could be obtained with fewer fractions, using the refractive index to determine the composition of each fraction. The separation of the products, obtained from alpha pinene, required the estimation of the recovered alpha pinene, the dipentene, and alloocimene plus its polymers. The amounts of pyronenes were so small that they required large samples and prolonged rectification to estimate their percentages, and for the purpose of this work they could properly be neglected. The problem reduced to the simple process of distilling off all the alpha pinene, boiling point 52° and 20 mm, at reflux ratios of about 5 to 1 and taking all the intermediate fraction and enough dipentene (boiling point 71°), to completely carry all the alpha pinene into the receiver without carrying over any alloocimene (boiling point 88°). The second fraction contained all the rest of the dipentene and the intermediate fraction of dipentene and alloocimene, care being taken that all the dipentene was in the receiver. From the weights and refractive indices of these fractions and the residue, the amounts of alpha pinene, dipentene, and alloocimene plus polymer were determined. Fuguitt showed that the refractive index of mixtures of alpha pinene and dipentene was a straight line function of the weight percent composition, and that alloocimene-dipentene mixtures showed essentially a similar relationship. The residue was substantially all alloocimene and dimers. More fractions were sometimes taken but this was the minimum required to make the necessary calculations.

The separation of the products of beta pinene was somewhat more difficult. Careful fractionation repeatedly failed to show the presence of appreciable amounts of myrcene as indicated by refractive index and boiling point. This left only recovered beta pinene, b.p. 60°, limonene, b.p. 71° and polymers b.p., 185° to be seperated. The same type of estimation as with alpha pinene was used. The refractive index of a mixture of limonene and beta pinene was found to be a straight line function of the composition, as shown by the following data:

	n_D^{25} observed	n_D^{25} interpolated
Limonene sample	1.4706	---
Beta Pinene sample	1.4763	---
40.4% Beta Pinene	1.4729	1.4729
61.5% Beta Pinene	1.4741	1.4741

There was no material like alloocimene boiling at a convenient temperature above the limonene which could be used to sweep out all the limonene. To remove the last few percent the polymer itself had to be boiled. The boiling point of this polymer was even higher than that of alloocimene dimer, so resort was made to the column built for alloocimene-dimer separation after the long, more efficient column had removed the beta pinene from the pot without distilling all the limonene. Even with considerable care, the use of two different columns introduced uncertainties into the ratio of limonene and polymer in the sample. Where the amounts of each were small, an attempt was made only to recover all the beta pinene.

Refractive indices of fractions were taken immediately after removal of the mixtures from the distilling heads, because brief exposure to air before storage under nitrogen seemed to produce some variation in results. All refractive indices refer to the sodium D line and almost all were made at 25°.

To make the operation simpler, all distillations were carried out at about 20 mm pressure.

APPENDIX II

CALCULATIONS FOR ISOMERIZATION OF THE PINENES

Alpha Pinene

The data from the analytical distillations (at 20 mm pressure) consisted of temperature range, refractive index, and weight of distillate fractions; original weights of pot samples; and weights of residues. The first fraction contained alpha pinene, boiling at 52°, and having $n_D^{25} = 1.4631$, and perhaps some dipentene, boiling at 71° and $n_D^{25} = 1.4701$ or 1.4702. Subsequent fractions contained either dipentene and alpha pinene or dipentene and alloocimene, which boils at 88° and has a $n_D^{25} = 1.5420$.

In the data from Experiment 112 in Table 22, page 109, the fractions were cut at such points that essentially pure alpha pinene and limonene fractions were obtained. This was not typical. Experiment H 116 demonstrates the usual procedure. The original pot sample contained 31.3 g dipentene plus the products obtained by heating 24.9 g of alpha pinene. The first fraction, to 70° on the thermometer used, weighed 16.7 grams and contained alpha pinene and dipentene. The refractive index of the fraction was 1.4640. Hence the percent of the products from the alpha pinene reaction, contained in this fraction are

$$\frac{16.7}{29.4} \times \frac{1.4640 - 1.4631}{1.4701 - 1.4631} \times 100 = 5.7\% \text{ dipentene}$$

and $$\frac{16.7}{29.4} \times \frac{1.4701 - 1.4640}{1.4701 - 1.4631} = 51.1\% \text{ alpha pinene.}$$

The dipentene in this first fraction came partly from the alpha pinene and partly from the dipentene used to dilute the original sample of alpha pinene.

The refractive index of the second fraction, which weighed 38.3 g., was 1.4702. This indicates that it was essentially pure dipentene as the literature value is 1.4701-2. Subtracting the weight of dipentene originally added from the weight of dipentene in this sample leaves the weight of the remainder of the dipentene formed from the alpha pinene. This, divided by the weight of the alpha pinene sample and multiplied by a hundred gives the percent of the original sample of alpha pinene which appears as dipentene in this fraction.

$$\frac{38.3 - 31.3}{29.4} \times 100 = 23.8\%$$

The total dipentene obtained from alpha pinene is therefore 23.8 + 5.7 = 29.5%.

Alloocimene is viscous and easily oxidized to a gum. It has been shown (15) that upon distillation an appreciable amount is lost in the distilling column and head due probably to oxidation and polymerization. For this reason the unaccounted for material was included in the amount of alloocimene formed. As will be seen in Experiment H 116, there was a difference of 0.2 g. between pot sample and products. This was added to the weighed residue and together they amounted to 19.4% of the weight of alpha pinene originally used. The same result is obtained by subtracting the percentages of alpha pinene and limonene from 100%.

As can be shown (16), the sum of the reaction rate constant k_1, for the unimolecular reaction to dipentene, plus k_2, for the production of alloocimene, is given by

$$k_1 + k_2 = \frac{2.3}{t} \log \frac{100}{\%\text{ recovered alpha pinene}} .$$

For experiment H 116

$$k_1 + k_2 = \frac{2.3}{2200} \log \frac{100}{51.1} = 0.00030 \text{ or } 3.0 \times 10^{-5}$$

The ratio of dipentene to alloocimene plus its polymers was 29.5/19.4, so $k_1 / k_2 = 1.52$. From thus $k_1 = 1.8 \times 10^{-5}$, and $k_2 = 1.2 \times 10^{-5}$. This result is included in Table 1, page 12.

Beta Pinene

This decomposes in a manner somewhat similar to that of alpha pinene. The calculations are of the same type, and a similar presentation of the date is used in Table 23, page 117. The quantity $k_1 + k_2$ was again the one desired, and k_1 and k_2 were calculated from the ratio of limonene to polymers. This ratio was only determined for a limited number of experiments because experimental difficulties made it tedious and uncertain where only small amounts of dipentene were formed.

The calculations involved in Experiment H 165, page 118, are given for purposes of illustration. Beta pinene boiled at 60° at 20 mm and had an n_D^{25} of 1.4764. Dipentene and 1-limonene again had a boiling point of 71° at 20 mm and $n_D^{25} = 1.4701$-2. The polymers had a boiling point of 185° and $n_D^{25} = 1.500$.

The first fraction here amounted to 54% of the original sample or 51.5% beta pinene and 2.5% limonene based on the original sample. The second fraction also contained both components, 3.0% beta pinene and 11.5% limonene, based on the original sample. The residues made up the remainder of 100%, and were considered to be produced from myrcene.

$$k_1 + k_2 = \frac{2.3}{2900} \log \frac{100}{54.5} = 0.00021$$

k_1/k_2 = limonene/residues = 14.0/31.5 = 0.445.

This result is shown in Table 6, page 22. The average value of k_1/k_2 is used with the average for $k_1 + k_2$ to obtain the individual values of k_1 and k_2 shown in the same table.

TABLE 22

ESTIMATION OF PRODUCTS FROM ALPHA PINENE ISOMERIZATION

B.P. (20mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% alpha pinene	% Limonene	% allo-ocimene + polymers
Calculations for Table 1, page 12						
H 112 (61.1 g Sample: 31.6 g limonene and 29.5 g from alpha pinene)						
to 66°	1.4631-2	22.5		76.3		
to 78°	1.4702	35.8			14.2	
Residue		2.6				9.5
Totals		60.9		76.3	14.2	9.5
H 113 (70.2 g Sample: 36.2 g limonene and 34.0 g from alpha pinene)						
to 66°	1.4632	25.4		73.7	1.1	
to 78°	1.4702	41.1			14.4	
Residue		3.2				10.8
Totals		69.7		73.7	15.5	10.8
H 116 (60.7 g Sample: 31.3 g limonene, 29.4 g from alpha pinene)						
to 70°	1.4640	16.7		51.1	5.7	
to 80°	1.4702	38.3			23.8	
Residue		5.5				19.4
Totals		60.5		51.1	29.5	19.4
H 117 (59.5 g Sample: 30.7 g limonene and 28.8 g from alpha pinene)						
to 68°	1.4632	14.2		49.0	0.7	
to 80°	1.4710	40.2			30.9	0.6
Residue		4.6				18.8
Totals		59.0		49.0	31.6	19.4

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate		% alpha Pinene	% Limonene	% allo-ocimene + polymers
		Wt. g	% of Sample			
H 114 (84.0 g Sample: 43.4 g limonene and 40.6 g from alpha pinene)						
to 65°	1.4631	13.2		32.3		
to 71°	1.4716	43.9				2.3
to 80°	1.4710	17.7			42.1	0.5
Residue		8.8				22.8
Totals		83.6		32.3	42.1	25.6
H 115 (61.4 g Sample: 31.7 g limonene and 29.7 g from alpha pinene)						
to 68°	1.4635	9.7		30.8	1.9	
	1.4730	46.0			41.8	6.2
Residue		5.4				19.3
Totals		61.1		30.8	43.7	25.5
H 52 (103.3 g Sample: 52.7 g limonene and 50.6 g from alpha pinene)						
to 61°	1.4636	9.0		16.5	1.3	
to 72°	1.4727	2.8			5.3	0.2
to 78°		74.3			42.6	
Residue		16.4				32.5
Totals		102.5		16.5	49.2	32.7
H 53 (104.2 g Sample: 53.1 g limonene and 51.1 g from alpha pinene)						
to 71°	1.4670	12.7		11.0	13.9	
to 78°		72.9			38.5	
Residue		17.4				36.6
Totals		103.0		11.0	52.4	36.6

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate		% alpha Pinene	% Limonene	% allo-ocimene + polymers
		Wt. g	% of Sample			
Calculations for Table 2, page 14						
H 152 (34.0 g of alpha pinene)						
to 66°	1.4640	13.5	39.7	34.6	5.1	
to 71°	1.4713	4.1	12.0		11.8	0.2
to 88°	1.4801	10.7	31.5		27.1	4.4
Residue		5.4				16.8
Totals		33.7		34.6	44.0	21.4
H 153 (33.6 g of alpha pinene)						
to 56°	1.4640	13.0	38.7	33.7	5.0	
to 67°	1.4663	1.3	3.9	2.1	1.8	
to 71°	1.4707	10.6	31.6		31.3	0.3
to 88°	1.4893	2.5	7.4		5.4	2.0
Residue		6.3				18.4
Totals		33.7		35.8	43.5	20.7
H 58 (63.7 g of alpha pinene)						
to 60°	1.4645	7.7	12.1	9.7	2.4	
to 71°	1.4710	4.1	6.4		6.3	0.1
to 80°	1.4702	29.3	46.0		45.9	0.1
Residue		23.0				35.5
Totals		64.1		9.7	54.6	35.7
H 59 (51.4 g of alpha pinene)						
to 60°	1.4642	6.3	12.2	10.3	1.9	
to 70.5°	1.4709	2.5	4.9		4.9	
to 85°		24.9	48.4		48.4	
Residue		17.7	34.5			34.5
Totals		51.4		10.3	55.2	34.5

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% alpha Pinene	% Limonene	% allo-ocimene + polymers
Calculations for Table 3, page 14						
H 64 (57.3 g a pinene)						
to 68°	1.4632-3	33.1	57.8	56.6	1.2	
to 84°		12.5	21.8		21.8	
Residue		11.1				20.4
Totals		56.7		56.6	23.0	20.4
H 154 (34.3 g a pinene)						
to 66°	1.4649	14.9	43.5	32.3	11.2	
to 66°	1.4685	0.7	2.0	0.5	1.5	
to 70°	1.4709	3.8	11.1		11.0	0.1
to 88°	1.4778	8.8	25.7		22.9	2.8
Residue		5.9				17.7
Totals		34.1		32.8	46.6	20.6
H 65 (61.8 g a pinene)						
to 55°	1.4637	11.5	18.6	17.0	1.6	
to 67°	1.4694	1.2	1.9	0.2	1.7	
to 72°	1.4711	1.5	2.4		2.4	
to 84°		27.1	43.8		43.8	
Residue		20.3				33.3
Totals		61.6		17.2	49.5	33.3
H 155 (33.6 g a pinene)						
to 56°	1.4650	6.0	17.9	13.0	4.9	
to 67°	1.4708	1.0	3.0		3.0	
to 70.5°	1.4717	10.6	31.6		30.9	0.7
to 88°	1.4778	7.4	22.0		19.6	2.4
Residue		8.4				22.4
Totals		33.4		13.0	58.4	25.5

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate		% alpha Pinene	% Limonene	% allo-ocimene + polymers
		Wt. g	% of Sample			
Calculations for Table 4, page 15						
H 56 (63.6 g alpha pinene)						
to 70°	1.4637	35.4	55.7	55.2	0.5	
to 71°	1.4712	1.9	3.0		3.0	
	1.4738	13.6	21.4		20.2	1.2
Residue		12.0				19.9
Totals		62.9		55.2	23.7	21.1
H 57 (57.9 g alpha pinene)						
to 70.5°	1.4640	34.3	59.3	58.5	0.8	
to 85°		12.4	21.4		21.4	
Residue		11.6				19.3
Totals		58.3		58.5	22.2	19.3
H 38 (72.4 g alpha pinene)						
to 54°	1.4632	7.1	9.7	9.6	0.1	
to 69°	1.4678	3.7	5.1	1.7	3.4	
to 85°		38.1	52.1		52.1	
Residue		23.1				33.1
Totals		72.0		11.3	55.6	33.1
H 39 (53.1 g alpha pinene)						
to 56°	1.4652	0.8	1.5	1.0	0.5	
to 69°	1.4730	0.8	1.5		1.4	0.1
to 71°	1.4718	1.5	2.8		2.7	0.1
to 82°	1.4704	28.0	52.7		52.5	0.2
to 88°	1.5231	1.6	3.0		0.8	2.2
Residue		17.7				38.5
Totals		50.4		1.0	57.9	41.1

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% alpha Pinene	% Limonene	% allo-ocimene + polymers
H 40 (53.3 g alpha pinene)						
to 54°	1.4648	1.1	2.1	1.6	0.5	
to 68°		2.0	3.8		3.8	
to 85°	1.4705	30.0	56.3		56.0	0.3
85° up		2.5	4.7			4.7
Residue		17.2				33.1
Totals		52.8		1.6	60.3	38.1
H 60 (58.2 g alpha pinene)						
to 70°	1.4642	8.0	13.8	11.6	2.2	
to 80°		27.8	47.8		47.8	
Residue		20.2				38.4
Totals		56.0		11.6	50.0	38.4
H 61 (54.8 g alpha pinene)						
to 60°	1.4641	7.2	13.1	11.2	1.9	
to 70°	1.4710	2.2	4.0		3.9	0.1
to 81°		26.4	48.2		48.2	
Residue		18.6				34.7
Totals		54.4		11.2	54.0	34.8

Calculations for Table 5, page 16

B.P. (20mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% alpha Pinene	% Limonene	% allo-ocimene + polymers
H 24 (54.4 g alpha pinene)						
to 69°	1.4641	12.6	23.2	19.9	3.3	
to 84°		27.7	51.0		51.0	
Residue		13.4				25.8
Totals		53.7		19.9	54.3	25.8

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% alpha Pinene	% Limonene	% allo-ocimene + polymers
H 25 (54.2 g alpha pinene)						
to 60°	1.4638	11.6	21.4	19.3	2.1	
to 72°	1.4696	3.0	5.5	0.4	5.1	
to 80°		26.7	49.2		49.2	
Residue		12.9				23.9
Totals		54.2		19.7	56.4	23.9
H 54 (96.5 g alpha pinene)						
to 60°	1.4644	9.4	9.8	7.6	1.8	
to 70°	1.4709	5.3	5.6		5.6	
to 71.7°		44.4	46.5		46.5	
to 85°		5.3	5.6		5.6	
Residue		31.8				32.9
Totals		96.2		7.6	59.5	32.9
H 55 (65.3 g alpha pinene)						
to 62°	1.4648	5.7	8.7	6.6	2.1	
to 71°	1.4702	3.2	4.9		4.9	
to 85°		33.3	51.0		51.0	
Residue		22.7				35.4
Totals		64.9		6.6	58.0	35.4
H 62 (48.3 g alpha pinene)						
to 60°	1.4640	9.5	19.7	17.2	2.5	
to 72°	1.4707	1.7	3.5		3.5	
to 80°		21.6	44.7		44.7	
Residue		14.9				32.1
Totals		47.7		17.2	50.7	32.1

TABLE 22 (Continued)

B.P. (20mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% alpha Pinene	% Limonene	% allo-ocimene + polymers
H 63 (48.4 g alpha pinene)						
to 62°	1.4640	9.6	19.8	17.3	2.5	
to 72°	1.4709	4.3	8.9		8.9	
to 82°		18.4	38.0		38.0	
Residue		15.9				33.3
Totals		48.2		17.3	49.4	33.3
H 66 (78.4 g alpha pinene)						
to 70°	1.4639	19.5	24.9	22.1	2.8	
to 81°		39.4	50.3		50.3	
Residue		19.4				24.8
Totals		78.3		22.1	53.1	24.8
H 67 (70.0 g alpha pinene)						
to 60°	1.4639	14.4	20.6	18.2	2.4	
to 72°	1.4709	1.6	2.3		2.3	
to 84°		29.9	42.7		42.7	
Residue		22.6				33.4
Totals		68.5		18.2	47.4	33.4

TABLE 23

ESTIMATION OF PRODUCTS FROM BETA PINENE ISOMERIZATION

B.P. (20 mm)	n_D^{25}	Distillate		% beta Pinene	% Limonene	% Polymers
		Wt. g	% of Sample			
Calculations for Table 6, page 22						
H 161 (41.7 g Sample)						
to 66°	1.4768	34.5	82.8	82.8		
to 72°	1.4747	2.0	4.8	3.5	1.3	
Residue		4.8				
Totals		41.3		86.3		
H 162 (41.3 g Sample)						
to 66°	1.4768	33.9	82.1	82.1		
to 72°	1.4731	1.8	4.4	2.1	2.3	
Residue		5.0				
Totals		40.7		84.2		
H 163 (42.2 g Sample)						
to 66°	1.4762	30.3	71.8	69.5	2.3	
to 80°	1.4723	3.8	9.0	3.1	5.9	
Residue		7.8				
Totals		41.9		72.6		
H 164 (41.9 g Sample)						
to 66°	1.4762	29.9	71.4	69.1	2.3	
to 80°	1.4724	3.9	9.3	3.4	5.9	
Residue		8.1				
Totals		41.9		72.5		

TABLE 23 (Continued)

B. P. (20 mm)	n_D^{25}	Distillate		% beta Pinene	% Limonene	% Polymers
		Wt. g	% of Sample			
H 165 (42.1 g Sample)						
to 66°	1.4761	22.7	54.0	51.5	2.5	
to 80°	1.4714	6.1	14.5	3.0	11.5	
Residue		13.2				31.5
Totals		42.0		54.5	14.0	31.5
H 166 (42.1 g Sample)						
to 66°	1.4760	22.6	53.6	50.2	3.4	
to 80°	1.4720	6.3	15.0	4.5	10.5	
Residue		13.0				31.4
Totals		41.9		54.7	13.9	31.4
H 167 (41.6 g Sample)						
to 66°	1.4754	15.0	36.0	30.3	5.7	
to 80°	1.4713	7.8	18.7	3.6	15.1	
Residue		18.7				45.3
Totals		41.5		33.9	20.8	45.3
H 168 (41.4 g Sample)						
to 65°	1.4762	12.3	29.7	28.8	0.9	
to 80°	1.4720	10.0	24.2	7.3	16.9	
Residue		19.2				46.1
Totals		41.5		36.1	17.8	46.1

Calculations for Table 7, page 22

H 214 (55.6 g Sample)						
to 62°	1.4760	50.0		84.5	5.4	
to 72°	1.4717	0.9		0.5	1.1	
Residue		4.2				
Totals		55.1		85.0		

TABLE 23 (Continued)

B.P. (20 mm)	n_D^{25}	Distillate		% beta Pinene	% Limonene	% Polymers
		Wt. g	% of Sample			
H 215 (58.5 g Sample)						
to 62°	1.4759	53.1		84.0	6.9	
to 72°	1.4728	1.7		1.3	2.0	
Residue		3.3				
Totals		58.1		85.3		
H 216 (52.4 g Sample)						
to 72°	1.4757	42.7		73.0	8.7	
to 72°	1.4705	1.1		0.2	1.9	
Residue		8.3				
Totals		52.1		73.2		
H 217 (53.9 g Sample)						
to 65°	1.4757	41.5		68.8	8.2	
to 72°	1.4726	3.5		2.8	3.7	
Residue		8.4				
Totals		53.4		71.6		
H 209 (34.0 g Sample)						
to 72°	1.4753	20.5	60.4	49.9	11.5	
to 80°	1.4731	1.7	5.0	2.4	2.6	
Residue		11.7				33.6
Totals		33.9		52.3	14.1	33.6
H 210 (34.3 g Sample)						
to 72°	1.4750	21.65	63.2	49.1	14.1	
to 100°	1.4805	1.4	4.1		2.7	1.4
Residue		10.9				32.7
Totals		33.95		49.1	16.8	34.1

TABLE 23 (Continued)

B.P. (20 mm)	n_D^{25}	Distillate				
		Wt. g	% of Sample	% beta Pinene	% Limonene	% Polymers
H 211 (33.3 g Sample)						
to 72°	1.4741	15.9	47.7	30.3	17.4	
to 80°	1.4712	2.0	6.0	1.0	5.0	
Residue		15.0				46.3
Totals		32.9		31.3	22.4	46.3
H 212 (33.2 g Sample)						
to 72°	1.4747	13.9	41.9	30.6	11.3	
to 80°	1.4709	4.2	12.6	1.6	11.0	
Residue		14.9				45.5
Totals		33.0		32.2	22.3	45.5

Calculations for Table 8, page 24

H 169 (83.5 g Sample containing 41.9 g beta pinene products)				
to 63°	1.4765	34.5		82.5
to 65°	1.4710	2.1		0.7
Residue		46.1		
Totals		82.7		83.2
H 170 (83.9 g Sample containing 42.1 g beta pinene products)				
to 63°	1.4765	29.3		69.6
to 65°	1.4712	2.5		1.0
Residue		51.0		
Totals		82.8		70.6
H 171 (84.7 g Sample containing 42.5 g beta pinene products)				
to 63°	1.4762	22.5		51.3
to 71°	1.4704	2.1		0.2
Residue		59.7		
Totals		84.3		51.5

TABLE 23 (Continued)

B.P. (20 mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% beta Pinene	% Limonene	% Polymers
H 172 (83.9 g Sample containing 42.1 g beta pinene products)						
to 63°	1.4766	14.5		34.5		
to 65°	1.4703	4.0		0.1		
Residue		64.4				
Totals		82.9		34.6		
Calculations for Table 9, page 24						
H 192 (33.5 g. beta pinene products)						
to 66°	1.4762	27.3		79.0		
to 72°	1.4702	1.9		0.1		
Residues		4.3				
Totals		33.5		79.1		
H 193 (33.3 g beta pinene products)						
to 66°	1.4761	23.7		67.9		
to 72°	1.4702	2.3		0.1		
Residue		7.0				
Totals		33.0		68.0		
H 194 (34.7 g Beta pinene products)						
to 66°	1.4760	18.2		49.1		
to 72°	1.4704	1.6		0.2		
Residue		14.5				
Totals		34.3		49.3		
H 195 (34.2 g beta pinene products)						
to 68°	1.4746	16.5		34.5		
Residue		17.3				
Totals		33.8		34.5		

TABLE 23 (Continued)

B.P. (20 mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% beta Pinene	% Limonene	% Polymers
H 196 (41.6 g beta pinene products)						
to 66°	1.4742	15.4		24.1		
Residue		26.1				
Totals		41.5		24.1		
H 197 (32.0 g beta pinene products)						
to 66°	1.4760	16.9		49.5		
to 72°	1.4721	0.9		0.9		
Residue		13.8				
Totals		31.6		50.4		

Calculations for Table 10, page 25

B.P. (20 mm)	n_D^{25}	Distillate Wt. g	Distillate % of Sample	% beta Pinene	% Limonene	% Polymers
H 198 (40.4 g beta pinene)						
to 69°	1.4752	23.4		47.0		
to 80°	1.4722	3.1				
Residue		13.5				
Totals		40.0		47.0		
H 199 (34.5 g beta pinene)						
to 66°	1.4765	27.5		79.8		
to 72°	1.4750	2.0		4.5		
Residue		4.5				
Totals		34.0		84.3		
H 200 (33.9 g beta pinene)						
to 72°	1.4759	25.3		68.9		
Residue		8.3				
Totals		33.6				

TABLE 23 (Continued)

B.P (20 mm)	n_D^{25}	Distillate		% beta Pinene	% Limonene	% Polymers
		Wt. g	% of Sample			
H 201 (34.3 g beta pinene)						
to 72°	1.4752	20.2		47.7		
Residue		13.8				
Totals		34.0				
H 202 (34.2 g beta pinene)						
to 72°	1.4751	15.8		36.7		
Residue		18.4				
Totals		34.2				
H 203 (33.2 g beta pinene)						
to 72°	1.4742	13.0		25.5		
Residue		19.9				
Totals		32.9				

TABLE 24

CALCULATION OF CONSTANTS FOR
ISOMERIZATION OF BETA PINENE TO LIMONENE AND MYRCENE

$$\log \frac{k_m}{k_n} = \frac{E}{2.3\ R} \frac{(T_m - T_n)}{(T_m\ T_n)}$$

$$\log k = \frac{-E}{2.3RT} + \log S$$

$$T_m = 219.5^{\circ}C = 492.6^{\circ}\ K$$

$$T_n = 234.5^{\circ}C = 507.6^{\circ}\ K$$

For Limonene Formation

$$E_1 = \frac{2.3\ R\ (492.6)(507.6)}{507.6 - 492.6} \log \frac{2.9x10^{-4}}{0.64x10^{-4}} = 50{,}000\ \text{cal/mol}$$

$$\log S_1 = -\log \frac{2.9\ x\ 10^{-4}}{60} + \frac{49{,}800}{2.3\ R\ 507.6} = 16.2$$

For Myrcene Formation

$$E_2 = \frac{2.3R\ (492.6)(507.6)}{507.6 - 492.6} \log \frac{6.1x10^{-4}}{1.46x10^{-4}} = 47{,}000\ \text{cal/mol}$$

$$\log s_2 = -\log \frac{6.1x10^{-4}}{60} + \frac{47200}{2.3R\ 507.6} = 15.4$$

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Biography

Harry Gage Hunt was born September 27, 1912 in Chicago, Illinois. He attended the public schools of Tulsa, Oklahoma, and graduated from the University of Tulsa in 1934 with a Bachelor of Science degree. He worked for the Sinclair-Prairie Oil Company in Kansas for a year as a chemist and for the University of Wisconsin for five years. He received his Master of Science from Wisconsin in 1940. From 1940 to 1946 he worked for the Aluminum Research Laboratories at New Kensington, Pennsylvania, and at East St. Louis, Illinois.

Mr. Hunt was the holder of a Graduate Naval Stores Research Assistantship at the University of Florida from 1946 to 1950. He is a member of Phi Lambda Upsilon and Gamma Sigma Epsilon, the honorary Chemical societies; the Florida Academy of Science; American Association for the Advancement of Science; American Chemical Society; and the Electron Microscope Society of America.

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Date June 5, 1950

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